PB90-212564

Mobility and Degradation of Residues at Hazardous Waste Land Treatment Sites at Closure

Texas Univ. at Austin

Prepared for:

Robert S. Kerr Environmental Research Lab., Ada, OK

Apr 90

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-90/018	2.	3. RECIPIENT'S ACCESSION NO. PB90 212564/AS
4. TITLE AND SUBTITLE MOBILITY AND DEGRADATION OF RESIDUES AT HAZARDOUS WASTE LAND TREATMENT SITES AT CLOSURE		5. REPORT DATE 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Raymond C. Loehr, David C. Erickson, Laura A. Rogers, and Daniel M. Kelmar		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Engineering Program The University of Texas at Austin Austin, Texas 78712		10. PROGRAM ELEMENT NO. CBWD1A 11. CONTRACT/GRANT NO. CR-814490
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Laboratory - Ada, OK U.S. Environmental Protection Agency P.O. Box 1198 Ada, Oklahoma 74820		13. TYPE OF REPORT AND PERIOD COVERED Final Report (9/87 - 4/90) 14. SPONSORING AGENCY CODE EPA/600/15

15. SUPPLEMENTARY NOTES

Project Officer: Scott G. Huling FTS: 743-2313

16. ABSTRACT

Soil treatment systems that are designed and managed based on a knowledge of soil-waste interactions may represent a significant technology for simultaneous treatment and ultimate disposal of selected hazardous wastes in an environmentally acceptable manner. These soil treatment systems cease operations for various reasons and undergo a "closure process." This process is performed to minimize the long-term migration of waste constituents from the soil treatment system. Decisions pertaining to the closure process often center around the various closure scenarios. There is currently a lack of scientifically derived fate and transport information for the wide range of hazardous chemicals for which such decisions can be made. This report presents information pertaining to the quantitative evaluation of mobility and persistence of organic and inorganic waste constituents which have accumulated over a long-term period in soil treatment systems under various closure scenarios. This information will be useful in the development of soil treatment closure decisions which will be protective of human health and the environment.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO THE PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

PB90-212564

EPA/600/2-90/018
April 1990

MOBILITY AND DEGRADATION OF RESIDUES AT HAZARDOUS WASTE LAND TREATMENT SITES AT CLOSURE

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REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreement CR-814490 to The University of Texas at Austin. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

EPA is charged by Congress to protect the Nation's land, air, and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on groundwater, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

Soil treatment systems that are designed and managed based on a knowledge of soil-waste interactions may represent a significant technology for simultaneous treatment and ultimate disposal of selected hazardous wastes in an environmentally acceptable manner. These soil treatment systems cease operations for various reasons and undergo a "closure process". This process is performed to minimize the long-term migration of waste constituents from the soil treatment system. Decisions pertaining to the closure process often center around the various closure scenarios. There is currently a lack of scientifically derived fate and transport information for the wide range of hazardous chemicals for which such decisions can be made. This report presents information pertaining to the quantitative evaluation of mobility and persistence of organic and inorganic waste constituents which have accumulated over a long-term period in soil treatment systems under various closure scenarios. This information will be useful in the development of soil treatment closure decisions which will be protective of human health and the environment.

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ABSTRACT

The objectives of this project were to determine: (a) to what extent organics remaining at HWLT sites at closure continue to degrade, (b) the migration potential of the accumulated waste residue constituents, and (c) whether EPA models (RITZ and MINTEQ) are appropriate for closure decisions. These objectives were achieved by: (a) obtaining representative soil samples from the zone of incorporation (ZOI) and from the treatment zone of several HWLT sites and a related site, (b) characterizing the quantity and type of residual material in such samples, (c) conducting laboratory studies to determine the degradation and potential mobility of the constituents in the samples, and (d) using RITZ and MINTEQ to evaluate the migration potential of the residual constituents under different closure options. Soils used in the laboratory studies were obtained from three sites to which listed refinery or wood preserving wastes had been applied and from a site which had soil contaminated with coal tar.

In the surface soils of the HWLT sites, the concentration of the organics and metals were greater than in background soils. At depths below 24" at the HWLT sites, the concentrations of PAH compounds were below detection limits. For the sites at which site soil concentrations could be compared to in background soils, the concentrations of chromium and nickel in site soils at depths below 24" appeared greater than background soil concentrations whereas the concentrations of copper, lead and zinc in site soils at such depths appeared comparable to those in background soils.

Analyses for organics in TCLP extracts of the soils indicated that no PAH compounds were extracted by this procedure from either weathered or non-weathered soils. In most of the site soil samples analyzed, the concentrations of metals in the TCLP extracts were close to or below detection limits of 0.1 mg/L.

The PAH and metal concentrations measured in the TCLP extracts from the site soils provided no reason to conclude that these soils and accumulated residues would fail to pass a toxicity characteristic determination using the TCLP test.

The aerobic and anaerobic microcosm studies demonstrated that there was no statistically significant degradation of the PAH and freon extractables in the ZOI

samples over an eight-month period. The data suggest slow degradation of the accumulated organics following closure of a HWLT site.

MINTEQ is a predictive model that estimates aqueous equilibrium solubility concentrations for metals. However, gaps in the MINTEQ database do not allow it to identify the relative solubility of many of the metals of interest at HWLT sites. Thus, MINTEQ appears of limited value to identify the environmental fate of metals under different closure options.

When used with worst-case data for a petroleum refinery HWLT site, the modified RITZ indicated major differences in mobility and persistence of PAH compounds between capped and uncapped closure scenarios. The closure options in which the sites were uncapped allowed for more rapid degradation, but movement of the constituents below the ZOI was greater. For the clay or synthetic cap option, the degradation of the organic constituents was much slower, but the movement below the ZOI diminished. This simulation indicated that the modified RITZ can be a useful tool for assessing the impact of different closure options on accumulated residuals at HWLT sites.

Based on the low migration potential of PAH compounds and metals at the HWLT sites, as measured and simulated in this study, it does not appear necessary to cap such sites at closure.

TABLE OF CONTENTS

Page

NOTICE ii

FOREWORD iii

ABSTRACT v

FIGURES x

TABLES xi

ACKNOWLEDGEMENTS xvi

SECTION 1. INTRODUCTION 1
  Scope of Study 1
  Background 5

SECTION 2. CONCLUSIONS 7
  Site Soil-Residue Characteristics 8
  Sample Variability 8
  Mobility and Weathering Studies 8
  Degradation Studies 9
  Predictive Models for Closure 9
  Closure Options 10

SECTION 3. SITES AND SOIL SAMPLES 11
  Land Treatment 11
  Sites and Soils 13
    Texaco 14
    Conoco 21
    Wood Treating (WTS) Site 27
    Niagara Mohawk Power Corporation (NMPC) 30

SECTION 4. GENERAL MATERIALS AND METHODS 33
  Introduction 33
  Microcosm Studies 33
  Analytical Procedures 36
  Gas Chromatography 36
  High Pressure Liquid Chromatography (HPLC) 36
  Flame Atomic Absorption Spectrophotometry 37
  Microtox Analysis 38

Page

Toxicity Characteristic Leaching Procedure . . . 39
Freon Extractables . . . 41
Percent Moisture . . . 41
Volatile Solids . . . 41

SECTION 5. SITE SOIL-RESIDUE CHARACTERISTICS . . . 42
Organics . . . 42
  Texaco (Anacortes) Site . . . 43
  Conoco (Ponca City) Site . . . 43
  Wood Treating (WTS) Site . . . 46
  Niagara Mohawk Power Corporation (NMPC) Site . . . 46
Metals . . . 47
  Texaco (Anacortes) Site . . . 47
  Conoco (Ponca City) Site . . . 50
  Wood Treating (WTS) Site . . . 52
  Niagara Mohawk Power Corporation (NMPC) Site . . . 54
Summary . . . 54

SECTION 6. SAMPLE VARIABILITY STUDIES . . . 55
Texaco . . . 56
Conoco . . . 56
Results . . . 60
  Variation Within Sites . . . 61
  Variation Among Test Plots . . . 64
Core Sample Representativeness . . . 65
Summary . . . 66

SECTION 7. MOBILITY AND WEATHERING STUDIES . . . 67
Background . . . 67
Estimating the Effect of Weathering . . . 70
Weathering Protocol . . . 71
  Freeze/Thaw Cycles . . . 73
  Wet/Dry Cycles . . . 75
    Quality Assurance/Quality Control . . . 75
  Analytical Procedures . . . 77
Results . . . 78
  Organics . . . 79
  Metals . . . 80
  Weathering Cycles . . . 82
Discussion . . . 83
  Migration Potential . . . 84
    Organics . . . 84
    Metals . . . 85
    Mass Balance . . . 86
  Hazardous Characteristics . . . 89
Conclusions . . . 90

Page

SECTION 8. DEGRADATION STUDIES 93
Results 93
Summary 98

SECTION 9. PREDICTIVE MODELS FOR CLOSURE 100
Introduction 100
Background 101
Computer Models 102
  Organics 102
  Inorganics 103
Closure Option Site Impacts 104
  Removal of Contaminated Soil 104
  Capping a Site 104
  Leave Site Alone 105
  Continued In-Situ Treatment 105
Model Modifications 105
  RITZ 105
  MINTEQ 108
Model Inputs and Outputs 109
  RITZ 109
  MINTEQ 112
Sensitivity to Parameters Influenced by Closure 117
  RITZ 117
  MINTEQ 128
Summary 139
  RITZ 141
  MINTEQ 141

SECTION 10. MODELING SPECIFIC SITES 143
Introduction 143
Texaco Anacortes 143
  Organics 144
    Site Data 144
    RITZ Results 147
  Metals 152
    Data 152
    MINTEQ Results 153
Other Sites 153
  Organics 154
  Metals 158
Summary 158
  RITZ 158
  MINTEQ 159
  Closure Options 159

SECTION 11. REFERENCES 161

LIST OF FIGURES

		Page
Figure 3.1	Schematic of a Typical Profile at a HWLT Site	12
Figure 3.2	Texaco Anacortes Sampling Locations	16
Figure 3.3	Top View of a Conoco Sampling Test Pit	23
Figure 3.4	Conoco Ponca City Research Site Sampling Locations	24
Figure 3.5	Wood Treating Site Test Pit Sampling Locations	29
Figure 3.6	Niagara-Mohawk Test Pit Sampling Locations	32
Figure 5.1	Average PAH Concentrations as a Function of Depth – Texaco, Anacortes Soil Samples	44
Figure 5.2	O/G (mg/kg) as a Function of Depth – Anacortes Test Pit B	44
Figure 5.3	Soil Metal Concentration (mg/kg dry weight) as a Function of Depth – Conoco (10% Site)	52
Figure 5.4	Nickel and Zinc Concentrations (mg/kg dry weight) in the WTS Soils as a Function of Depth	53
Figure 7.1	Summary of Test Procedures and Sequence Used in the Laboratory Weathering Studies	71
Figure 7.2	Outline of Steps and Sample Sizes Used in the Laboratory Weathering Studies	72
Figure 7.3	Example Gas Chromatograph Strip Chart Output of TCLP Extract, Conoco Site, 15% Plot, 6–12" Depth	80
Figure 7.4	TCLP Extract Metal Concentration (mg/L) as a Function of Depth – Conoco 10% Site	81
Figure 7.5	Soil Zinc Concentration (mg/L) as a Function of Depth – WTS Test Pits	82
Figure 7.6	Zinc Concentration in the Core Soil Samples from the Conoco 10% and 15% Sites	87
Figure 7.7	Zinc Concentration in the TCLP Extracts from the Core Soil Samples from the Conoco 10% and 15% Sites	88
Figure 9.1	Soluble Fraction of Metal as a Function of pH and PCO_2	138
Figure 9.2	Soluble Metal Concentrations as a Function of pH and PE	139

LIST OF TABLES

Page

Table 1.1 Options for the Closure of a HWLT Site 2

Table 1.2 Potential Impact of Closure Options on Site Soil Conditions and on Remaining Waste Constituents 2

Table 1.3 Hazardous Waste Identifications 3

Table 1.4 General Characteristics of the Field Sites from Which the Samples Used in this Study Were Obtained 4

Table 3.1 Soil Samples Were Taken of the Following Depths at the Respective Sites 13

Table 3.2 Wastes That Have Been Placed on the Texaco, Anacortes HWLT Unit 14

Table 3.3 Tons of Oil Applied to the East HWLT Plots at the Texaco, Anacortes HWLT Unit – 1980-1986 15

Table 3.4 Concentration (mg/kg) of Volatile and Acid Extractable Organics in Background Soils at the Texaco, Anacortes Land Treatment Site 17

Table 3.5 Average Total Metal Concentrations (mg/kg) in Soils at the Texaco, Anacortes Land Treatment Site 18

Table 3.6 Agronomic Parameters in Soils at the Texaco, Anacortes Land Treatment Site – 1985 Study 18

Table 3.7 Base Neutral Extractable Fraction (PAH) Compounds Detected in ZOI and LTZ Soils at the Texaco, Anacortes HWLT Site – 1985 Study 19

Table 3.8 Volatile Organics and Base Neutrals in Soils from the East HWLT Plots – Texaco, Anacortes – 1987 Study 20

Table 3.9 Amount of Waste Applied to the Conoco Research Site 23

Table 3.10 Average Background Soil Characteristics – Conoco, Ponca City Land Treatment Site – 1976 Data 25

Table 3.11 Average Metal Concentrations (mg/kg) in Background Soils – Conoco, Ponca City Land Treatment Site – 1976 Data 26

Table 3.12 Background Surface and Subsurface Soil Characteristics – Conoco, Ponca City Land Treatment Site – 1984 Data 25

Page

Table 3.13 Concentrations of Metals and Base Neutral Compounds in the K-001 Sludge Applied to the Wood Treating Site LTD Plot . . . 28

Table 3.14 Average Background ZOI characteristics--Wood Treating Site--1985 Data 30

Table 3.15 Metal Concentrations in Subsurface Soils from an Area Near the WTS Site 30

Table 4.1 Aerobic Batch Degradation Rate Procedure 34

Table 4.2 Anaerobic Batch Degradation Rate Procedure 35

Table 4.3 Characteristics of PAH Compounds Measured in this Study . . 35

Table 4.4 Operating Conditions for the Gas Chromatographic Analysis of Compounds in Methylene Chloride 37

Table 5.1 Treatment Processes That Can Occur in Soil 42

Table 5.2 PAH Concentrations at the Texaco Site as a Function of Depth . . 45

Table 5.3 PAH Concentrations at the Conoco Site (15% Plot) 46

Table 5.4 PAH Concentrations at the Conoco Site (Samples from the 0-6" Depth) 47

Table 5.5 PAH Concentrations at the WTS Site (mg/kg dry weight of soil) . . 48

Table 5.6 PAH Concentrations at the NMPC Site (mg/kg dry weight of soil) . 48

Table 5.7 Average Metal Concentrations in the Texaco, Anacortes Soil Core Samples (mg/kg dry weight of soil) 49

Table 5.8 Metal Concentrations (mg/kg) in the Soil Cores from this Study and in Background Soils – Texaco, Anacortes Site 49

Table 5.9 Metal Concentrations (mg/kg) in ZOI (0-12") Samples from this Study and from a Previous Study – Texaco, Anacortes Site . . . 50

Table 5.10 Average Metal Concentrations in the Core Soil Samples of the Conoco 5%, 10% and 15% Plots – (mg/kg dry weight of soil) . . 51

Table 5.11 Metal Concentrations (mg/kg dry weight) in Soil Cores from this Study and in Background Soils – Conoco Site 51

Table 5.12 Average Metal Concentrations in the WTS Soils (mg/kg dry weight of soil) 53

Table 5.13 Average Metal Concentrations in the NMPC Soils (mg/kg dry weight of soil) 54

Table 6.1 Solids and Oil and Grease in the ZOI Samples from the Texaco Site 56

Table 6.2 Copper, Chromium, and Iron Concentrations in the ZOI Samples from the Texaco Site 57

Table 6.3 Solids and Oil and Grease in the ZOI Samples from the 5% Conoco Site 57

Page

Table 6.4 Solids and Oil and Grease in the ZOI Samples from the 10% Conoco Site 58
Table 6.5 Solids and Oil and Grease in the ZOI Samples from the 15% Conoco Site 58
Table 6.6 Copper, Chromium, and Iron Concentrations in the ZOI Samples from the 5% Conoco Site 59
Table 6.7 Copper, Chromium, and Iron Concentrations in the ZOI Samples from the 10% Conoco Site 59
Table 6.8 Copper, Chromium, and Iron Concentrations in the ZOI Samples from the 15% Conoco Site 60
Table 6.9 Statistical Values for Parameters Analyzed in the ZOI of the Conoco 5, 10 and 15% Plots 61
Table 6.10 Summary of Conoco and Texaco ZOI Analyses 62
Table 6.11 ANOVA Results for the Conoco Plots 63
Table 6.12 Significant Differences Observed Between Sample Means – Conoco 5, 10 and 15% Plots 64
Table 6.13 Constituents in the ZOI Soils from the Spatial Variability and the Core Samples 65
Table 7.1 Influence of Atmospheric Variables on Land Treatment Processes 68
Table 7.2 Summary of Weathering Procedure Used 74
Table 7.3 Soil Samples Used for the Weathering Cycles 74
Table 7.4 Analyses Used With Specific Samples 76
Table 7.5 Metal Concentrations (mg/L) in TCLP Extracts of Soil Samples . . 77
Table 7.6 Average Metal Concentrations in the TCLP Extracts from the Conoco 10% Plot Site – Non-Weathered Samples 81
Table 7.7 Average Metal Concentrations in the TCLP Extracts from the NMPC Site – Non-Weathered Samples 82
Table 7.8 Average Metal Concentrations in the TCLP Extracts from the Conoco 10% Plot Site – Weathered Samples 83
Table 7.9 Metal Concentrations in the TCLP Extracts (mg/L) Weathered Samples 84
Table 7.10 Concentration (mg/L) of Metals in TCLP Extracts After Freeze/Thaw Cycles and Wetting/Drying Cycles 85
Table 7.11 Maximum Concentration of Contaminants for the Hazardous Waste Characteristics of Toxicity 91
Table 7.12 Maximum TCLP Extract Concentrations from this Study and Concentrations Indicating Toxicity Characteristics 92

Page

Table 8.1 Average PAH Concentrations in the Composite Texaco ZOI Soil – Aerobic Microcosm Study 95
Table 8.2 Average PAH Concentrations in the Composite Texaco ZOI Soil – Anaerobic Microcosm Study 96
Table 8.3 Average PAH Concentrations in the Composite Anacortes ZOI Soil – Aerobic Plus Nutrient Microcosm Study 96
Table 8.4 Freon Extractable Data in the Composite Texaco ZOI Soil – Aerobic and Anaerobic Loss Studies 97
Table 8.5 Analysis of Variance Summary of Degradation Data 98
Table 8.6 Q Test Evaluation of Mean PAH Concentrations 99
Table 8.7 Q Test Evaluation of Mean Freon Extractable Concentrations . . 99
Table 9.1 Brooks and Corey Parameters Used in RITZ 110
Table 9.2 Parameter Values Used in Examining RITZ Sensitivity to Temperature and Relative Humidity 118
Table 9.3 Sensitivity of Naphthalene Loss to Temperature Variations . . . 119
Table 9.4 Sensitivity of Naphthalene Loss to Relative Humidity Variations. . 120
Table 9.5 Fate and Transport Parameters Used in Analysis of Oil Phase Parameters 121
Table 9.6 Results of Oil Phase Analysis for a Loamy Sand 122
Table 9.7 Fate and Transport Values Used in Sensitivity Analysis 123
Table 9.8 Half-Depths in the LTZ and Associated γ Values 124
Table 9.9 Degradation Rate Depth Constant Variation and o-Xylene Mobility 124
Table 9.10 Sensitivity of o-Xylene Mobility to γ and f_{oc} Variation 125
Table 9.11 Half-Times and Associated ω Values 126
Table 9.12 Sensitivity of o-Xylene Mobility to Degradation Rate Time Variability 127
Table 9.13 Sensitivity of the Persistence of Anthracene and o-Xylene to the Decrease of the Degradation Rate With Time 127
Table 9.14 Degradation Rate Depth and Time Constants Associated With Each Closure Option 128
Table 9.15 Soil Solution Composition for a Holtsville Soil 129
Table 9.16 Changes in Metal Speciation and Soluble Metal Fractions as a Function of pH 132
Table 9.17 Fraction of Input Metal Concentration Remaining Soluble After Speciation 133
Table 9.18 Metal Speciation as Influenced by pH and the Presence of Organics 134

Page

Table 9.19 Dominant Aqueous Forms at pH 7.1 for $^{+2}$ Forms of Copper, Cadmium, Iron and Lead as a Function of PCO_2 136

Table 9.20 Dominant Aqueous Forms at pH 9 for $^{+2}$ Forms of Copper, Cadmium, Iron and Lead as a Function of PCO_2 137

Table 10.1 Parameters for Soil Textures Prevalent at Texaco, Anacortes HWLT Site 144

Table 10.2 Maximum Concentration of Volatile Organics and Base Neutrals Identified in Texaco, Anacortes HWLT Site Soil Cores 146

Table 10.3 Fate and Transport Parameters for Organic Constituents . . . 147

Table 10.4 Soil and Hydrologic Parameters Used in Worst-Case Modeling Efforts 148

Table 10.5 Modeling of the Texaco, Anacortes Site for the Leave-Alone Closure Option 149

Table 10.6 Modeling of the Texaco, Anacortes Site for the Closure Options of a Clay or Synthetic Cap 150

Table 10.7 Plot-Specific Parameters Used for Modeling of o-Xylene Mobility at the Texaco, Anacortes Site 151

Table 10.8 Plot-Specific Modeling of o-Xylene at the Texaco, Anacortes Site 151

Table 10.9 Metals Modeled at the Texaco, Anacortes Site 152

Table 10.10 Modeling of a Hypothetical New Jersey HWLT Site for the Leave-Alone Closure Option 154

Table 10.11 Modeling of a Hypothetical New Jersey HWLT Site for the Clay or Synthetic Cap Closure Option 155

Table 10.12 Modeling of a Hypothetical Louisiana HWLT Site for the Leave-Alone Closure Option 155

Table 10.13 Modeling of a Hypothetical Louisiana HWLT Site for the Clay or Synthetic Cap Closure Option 156

Table 10.14 Plot-Specific Modeling of o-Xylene Mobility at a Hypothetical New Jersey HWLT Site 156

Table 10.15 Plot-Specific Modeling of o-Xylene Mobility at a Hypothetical Louisiana HWLT Site 157

Table 10.16 Comparison of Organic Mobility for the Three Locations – Leave-Alone Option 158

Table 10.17 Comparison of Persistence and Mobility of Organics Present at the Texaco, Anacortes Site as Influenced by the Closure Option . 160

ACKNOWLEDGEMENTS

This report represents the hard work and dedication of the students and staff who assisted in this project. The contribution of the following individuals deserves specific recognition and is greatly appreciated:

Lisa Gilmour-Stallsworth
Nadine Gordon
Frank Hulsey
Lynn G. Sanders
Karen Spaniel
John Stephenson
Eric White

We also appreciate the assistance of the EPA-RSKERL project officers, Mr. John E. Matthews and Mr. Scott G. Huling. These individuals had responsibility for the project throughout its duration and provided valuable insights and assistance.

Cooperation and technical assistance were provided by the Niagara Mohawk Power Corporation (NMPC). The help and advice provided by Dr. Edward F. Neuhauser of NMPC is acknowledged and greatly appreciated.

Remediation Technologies, Inc. (ReTeC) collected the soil samples that were used in the laboratory experiments. The assistance and cooperation of Mr. John R. Ryan and Ms. June R. Coover of ReTeC in this valuable aspect of the project is much appreciated.

Recognition also should be made of help provided by many individuals from the several companies who allowed access to the sites, facilitated the sampling, and provided the background data on the site and the wastes that had been applied. Without their interest and cooperation, this project would not have been possible.

SECTION 1

INTRODUCTION

SCOPE OF STUDY

The process of land treatment has been used to treat municipal wastes for centuries. In addition, over the past thirty years there has been increased use of land treatment for industrial wastes, such as wastes from the petroleum industry. However, such wastes can contain constituents which are of potential concern to human health and the environment. With the passage of the 1984 Hazardous Solid Wastes Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA), there have been many changes in the regulatory framework with regard to the use of land based technologies for disposal of hazardous wastes. Due to the restrictions imposed by these regulations, there is an increase in the number of Hazardous Waste Land Treatment (HWLT) sites that are, or soon will be, undergoing closure. The organic and inorganic waste constituents that have accumulated at these sites can be of environmental concern due to: (a) potential mobility during the post-closure period, which can be as long as 30 years, and (b) the human and environmental exposure that might occur when the site is used after the post-closure period.

There are several major options (Table 1.1) for the closure of a land treatment site, or a site with contaminated soils, all of which involve the careful management of the site over the post-closure period, as defined by the regulations. Both direct and indirect impacts on human health and the environment are important in the selection of the site specific appropriate closure options. Each option will create different conditions in the site soil over time that will affect such impacts. Table 1.2 indicates how the closure options may affect soil conditions and their potential impact on the constituents remaining at closure.

The overall purpose of this project was to develop information pertaining to: (a) the characteristics of the waste constituents remaining at sites having long-term waste application, such as HWLT sites, and (b) the potential for subsequent degradation

TABLE 1.1 OPTIONS FOR THE CLOSURE OF A HWLT SITE(1)

- Removal of the contaminated soil and subsequent disposal of such soil as a hazardous waste
- Placement of an impermeable cap over the site. The cap may consist of synthetic liners or clay.
- The site is left alone with the only continued management being groundwater monitoring as well as run-on and runoff control and a vegetative cover.
- Continued managed in-situ treatment of the accumulated waste residues
- A combination of two or more of the above

TABLE 1.2 POTENTIAL IMPACT OF CLOSURE OPTIONS ON SITE SOIL CONDITIONS AND ON REMAINING WASTE CONSTITUENTS

Option	Impact on Soil Conditions	Impact on Constituents Remaining at Closure
Removal of Contaminated Soil	- may increase oxygen reaching lower depths - may create more oxidizing conditions for remaining soil - may enhance volatilization from lower depths - may remove surface organic matter	- source control, removes many constituents - increased aerobic degradation of organics
Placement of Impermeable Cap	- stop infiltration - greatly reduce oxygen diffusion to lower depths	- reduced conditions for chemical reactions - anoxic and anaerobic degradation of organics
Placement of Permeable Cap	- some decrease in oxygen diffusion - some reduction of infiltration	- aerobic and anoxic degradation of organics - some reduced conditions for chemical reactions
Sites Left Alone	- slight decrease in gas diffusion	- aerobic degradation of organics
Continued In-situ Treatment	- no major changes over operating conditions	- greater aerobic degradation of organics - oxidative conditions for chemical reactions

and/or migration of the constituents at such sites. Such information can help regulatory agencies and industry identify the most environmentally sound closure and post-closure conditions for a specific site and can help identify additional research needs related to the closure of HWLT sites.

Soil samples from four field sites were obtained for use in laboratory experiments. The sites were chosen based on the following criteria: (a) waste had been applied at the site for an extended period of time, preferably at least 10 years, or the waste treatment or disposal site had been closed (unused) for an extended period of time, (b) site history and background information were available, (c) the applied waste was representative of listed refinery wastes (K-048 to K-052) or of listed wood-preserving wastes (K-001), and (d) the site was available and accessible for sampling. Table 1.3 identifies these waste numbers with their specific sources and the characteristics for which the wastes were listed as hazardous.

A number of potential sites were considered but only a few met all the desired criteria. With the concurrence of the EPA-RSKERL project officer, three sites that met the criteria most closely were chosen. Soil from a fourth site that did not meet the criteria also was included in the project to expand the available knowledge about sites that contained constituents similar to those found in the listed wastes noted above.

TABLE 1.3 HAZARDOUS WASTE IDENTIFICATIONS(1)

EPA No.	Source Description	Compound(s) for Which Waste Is Listed
K001	bottom sediment sludge from treatment of wastewaters from wood-preserving processes that use creosote and/or pentachlorophenol	pentachlorophenol, phenol, 2- chlorophenol, p-chloro-m- cresol, 2,4-dimethylphenol, 2,4-dinitrophenol, tri- and tetrachlorophenols, creosote, chrysene, naphthalene, fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benz(a)anthracene, dibenz(a)anthracene, and acenaphthalene
K049	slop oil emulsion solids from the petroleum refining industry	hexavalent chromium, lead
K051	API separator sludge from the petroleum refining industry	hexavalent chromium, lead
K052	tank bottoms (leaded) from the petroleum refining industry	lead

The selected sites were: (a) the Texaco, Anacortes, Washington refinery land treatment site (petroleum refinery wastes), (b) a research site of Conoco at Ponca City, Oklahoma (petroleum refinery wastes), and (c) a wood treating site in Montana (wood-preserving wastes). In addition, the Niagara Mohawk Power Corporation (NMPC) cooperated in the project financially and by providing contaminated soil from a non-HWLT site in New York. The NMPC site was not a HWLT site and the results obtained from samples taken at this site should not be construed to represent conditions at a managed HWLT site. The NMPC site was included because: (a) it contained constituents similar to those in soils at the other sites -- metals, long-chain hydrocarbons, and polynuclear aromatic hydrocarbons (PAH) and (b) of the desire to expand the knowledge of sites containing similar constituents. The general characteristics of each site are described in Table 1.4.

TABLE 1.4 GENERAL CHARACTERISTICS OF THE FIELD SITES FROM WHICH THE SAMPLES USED IN THIS STUDY WERE OBTAINED

Characteristic	Texaco Anacortes	Conoco Ponca City	Wood Treating Site	Niagara Mohawk Power Corporation
Type of waste applied	petroleum refining process wastes and contaminated soil	petroleum refining process wastes	sludge from impoundment used for creosote contaminated wastewater	coal tar residues
Years site received waste	1958 to date	1976-1979	1985-1987	one disposal in 1960s
Operating status when samples taken	in operation	no waste applied after 1979	no waste applied after 1987	no operation-disposal only
Type of site when in operation	full-scale land treatment	research demonstration site	land treatment demonstration effort	trench disposal site
Site tilling frequency	when applied and intermittently	when applied and periodically through 1979	bi-weekly while in operation	none
General type of background soils	loamy sand acid pH	silt loam to silty clay loam acid pH	fine sandy loam acid pH	fine to coarse sand with some silt, acid pH
Average annual temperature (°F)	51	61	47	48
Mean annual precipitation (inches)	27	34	23	35

Studies were conducted to determine: (a) to what extent organics remaining at closure of such sites continue to degrade, (b) the migration potential of the accumulated waste residue constituents, and (c) whether EPA models (RITZ and MINTEQ) are appropriate for closure decisions.

BACKGROUND

All land disposal facilities must be designed, managed, and closed in a manner protective of human health and the environment. As part of the land disposal restrictions developed by EPA in response to HSWA , land disposal of hazardous waste will be limited to those wastes that can be treated to meet standards that are based on best demonstrated available technology (BDAT) or those that have undergone a successful petition process demonstrating that there will be no migration of hazardous constituents from the site for as long as the waste remains hazardous. These restrictions apply to hazardous waste land treatment facilities. Many such facilities, such as HWLT units that cannot meet these requirements, are expected to be closed.

Technical information is needed for both industry and regulatory agencies so that reasonable and environmentally sound closure plans and permits can be prepared. The current information base is inadequate to determine: (a) if the accumulated waste residues at a HWLT site represent a threat to human health and the environment and, (b) what happens to the remaining waste constituents at the site after closure, i.e., what are the long-term implications. To better understand the environmental fate of constituents that may exist when HWLT and similar land disposal sites are closed, this project:

(a) obtained representative soil samples from the four sites noted earlier;

(b) characterized the residual material in such samples;

(c) conducted laboratory studies to determine the degradation and potential mobility of constituents in the soil; and

(d) evaluated the migration potential of the residual constituents using several available EPA models.

The comparison procedures utilized throughout this research report to determine whether there is a significant difference between data populations are different than those typically employed using RCRA recommended procedures.

Therefore, the results of the comparison procedures used in this research report are expected to differ from those using RCRA guideline comparison procedures.

SECTION 2

CONCLUSIONS

There are several options for the closure of a hazardous waste land treatment site, or a site with contaminated soils. These include: (a) removal of the contaminated soil for subsequent disposal, (b) placement of a cap over the site using synthetic liners or clay or permeable soil, (c) leaving the site alone with continued groundwater monitoring, (d) continued in-situ management and treatment of the accumulated waste residues, and (e) a combination of the above. Each option will create different conditions in the soil at the site over time. Any attempt to understand and predict the fate of the contaminants at the site must include an evaluation of contaminant mobility and persistence under the closure conditions.

The objectives of this project were to determine: (a) to what extent organics remaining at HWLT sites at closure continue to degrade, (b) the migration potential of the accumulated waste residue constituents, and (c) whether EPA models (RITZ and MINTEQ) are appropriate for closure decisions. The following steps were undertaken to achieve these objectives:

(a) obtained representative soil samples from the zone of incorporation (ZOI) and from the treatment zone of several HWLT and related sites,

(b) characterized the quantity and type of residual material in such samples,

(c) conducted laboratory studies to determine the degradation and potential mobility of the constituents in the soil, and

(d) used RITZ and MINTEQ to evaluate the migration potential of the residual constituents under different closure options.

Soils used in the laboratory studies were obtained from three sites to which listed refinery or wood preserving wastes had been applied and from a site which had soil contaminated with coal tar.

The major results were the following.

SITE SOIL-RESIDUE CHARACTERISTICS

1. Polynuclear Aromatic Hydrocarbons (PAH), freon extractables, and metals were determined in the site soil samples. Except for the coal tar disposal site, these chemicals accumulated in the surface soils. The difference in the coal tar site data is due to the fact that the applied residues were placed in a trench rather than being incorporated in surface soils.

2. In the surface soils of the HWLT sites, the concentration of the organics and metals were greater than in background soils. At depths below 24" at the HWLT sites, the concentrations of PAH compounds were below detection limits and the freon extractable concentrations were at background soil concentrations or below detection limits. For the two sites for which soil metal concentrations could be compared to background soils, the concentrations of chromium and nickel in site soils at depths below 24" appeared greater than background soil concentrations whereas the concentrations of copper, lead and zinc in site soils at such depths appeared comparable to those in background soils.

SAMPLE VARIABILITY

3. At the two land treatment sites that were evaluated, there were no consistent differences in chemical concentrations of the surface soils. The analysis also indicated that the residues that existed at the time of sampling appeared to be uniformly distributed in the surface soils of each site.
4. Based upon a comparison of characteristics of soil samples at two petroleum industry land treatment sites, it appeared the core samples taken at these sites and used in the degradation and weathering studies were representative of the soils at these sites.

MOBILITY AND WEATHERING STUDIES

5. Analyses for organics in TCLP extracts indicated that no PAH compounds were extracted by this procedure from either weathered or non-weathered site soils.
6. There was no difference in the concentration of metals in the TCLP extract of the weathered and the non-weathered samples.
7. The results suggest that the type of weathering used in this study (freeze/thaw and wet/dry) is not expected to result in an increase in organic or metal mobility in soils at HWLT sites.

8. Zinc was found above detection limits in the TCLP extracts of the site soils most frequently. In most of the site soil samples analyzed, the concentration of metals in the TCLP extracts were close to or below detection limits of 0.1 mg/L.
9. The PAH and metal concentrations measured in the TCLP extracts from the site soils provided no reason to conclude that these soils and accumulated residues would fail to pass a toxicity characteristic determination using the TCLP test.

DEGRADATION STUDIES

10. The aerobic and anaerobic microcosm studies demonstrated that there was no statistically significant degradation of the PAH and freon extractables in the ZOI samples over an eight-month period. The data suggest, therefore, that there will be slow, rather than fast, degradation of the accumulated organics when HWLT sites are closed.

PREDICTIVE MODELS FOR CLOSURE

11. The RITZ model, as modified for HWLT site closure conditions, was insensitive to: (a) changes in relative humidity, (b) changes in temperature within the normal range found at HWLT sites, and (c) the oil phase parameters, both the initial oil content and the oil phase degradation rate. RITZ results showed some sensitivity to the soil type.
12. The sensitivity of MINTEQ was examined for parameters which are influenced by the closure option: pH, the partial pressure of carbon dioxide and the redox state. It was difficult to draw general conclusions about the effects of these changes, since different metals behave differently in solution. In general, most of the metals present in solution as cations became less soluble as the pH increased, and as the partial pressure of carbon dioxide increased. No general statements could be made about redox conditions, as the most soluble redox state of a given metal varies from metal to metal.
13. MINTEQ estimates aqueous equilibrium solubility concentrations for metals, however, gaps in the MINTEQ database do not allow it to identify the relative solubility of many of the metals of interest at HWLT sites. Thus, MINTEQ appears of limited value to identify the environmental fate of metals under different closure options.
14. When used with worst-case data for a petroleum refinery HWLT site, the modified RITZ indicated major differences in mobility and persistence of PAH compounds between capped and uncapped closure scenarios. The closure

options in which the sites were uncapped allowed for more rapid degradation, but movement of the constituents below the ZOI was greater. For the clay or synthetic cap option, the degradation of the organic constituents was much slower, but the movement below the ZOI diminished.

CLOSURE OPTIONS

15. Based on the low migration potential of PAH compounds, freon extractables and metals in the soils at HWLT sites, as determined from laboratory and model simulation studies, it does not appear necessary to cap such sites at closure. Both the leave-alone option, or the option to continue active site management, appear to be protective of human health and the environment.

SECTION 3

SITES AND SOIL SAMPLES

LAND TREATMENT

Prior to describing the actual sites from which the samples used in this study were taken, it is useful to discuss the land treatment process as used for industrial and particularly hazardous wastes. This discussion provides background for the information and results presented later in this report.

Land treatment is a process in which the physical, chemical and biological properties of a soil are used to immobilize and/or degrade constituents in a waste. The soil is a large treatment system. The waste is applied and the soluble fraction percolates through the soil in the aqueous phase. As liquid moves through the soil, constituents are removed through a combination of processes such as degradation and adsorption. Land treatment units are designed such that these processes occur in the top 1.5 meters of the soil, which is referred to as the treatment zone. This zone is divided into two areas, the top 0.3 meters, known as the zone of incorporation (ZOI) or the plow zone, and the remaining 1.2 meters, the lower treatment zone (LTZ). Figure 3.1 depicts a schematic of a HWLT site. A detailed description of hazardous waste land treatment is beyond the scope of this report and is available elsewhere(2-6).

Liquids, slurries and solids are applied to land treatment units. The inputs to the land treatment process include: (a) applied wastes (which are not applied after closure), (b) infiltration from precipitation as well as irrigation, and (c) run-on. The concentrations of constituents in rain water are negligible compared to those in the applied waste, and run-on can be eliminated with proper management. The outputs include: (a) run-off, which can be controlled through proper site management, (b) evapotranspiration, (c) percolation, and (d) volatilization, in which the constituents can leave the soil in the vapor phase.

Percolation or leaching of chemicals to groundwater is an environmental concern. At land treatment sites, this refers to the contaminants in the water which passes out the bottom of the LTZ. In HWLT there can exist an oil phase which moves

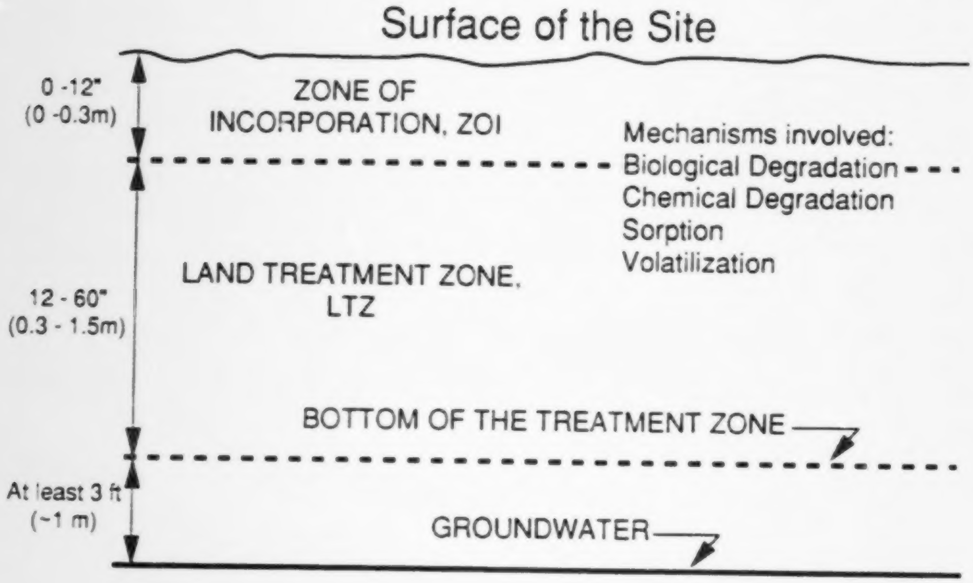
Surface of the Site
0 -12"
(0 -0.3m)
ZONE OF
INCORPORATION, ZOI
Mechanisms involved:
Biological Degradation
Chemical Degradation
Sorption
Volatilization
LAND TREATMENT ZONE,
LTZ
12 - 60"
(0.3 - 1.5m)
BOTTOM OF THE TREATMENT ZONE
At least 3 ft
(~1 m)
GROUNDWATER

FIGURE 3.1 SCHEMATIC OF A TYPICAL PROFILE AT A HWLT SITE

separately from the water phase. The oil phase generally is retained in the surface/ soils. However, at grossly mismanaged sites, an oily phase could occur at lower depths in land treatment units.

In soil, many processes can remove applied constituents that have the potential to leach. The two classes of constituents, organics and inorganics, are affected differently. Organics can be degraded either biologically or chemically into simple compounds, such as CO_2 or water, or transformed by similar processes into less oxidized compounds. The organics also can be retained in the soil by adsorption or complexation. Volatilization can play a role in the removal of some organics.

The processes for removal of inorganics are somewhat different. The potential concern is related to the mobility of the inorganics. There are many mechanisms by which inorganics are retained in the soil. These include adsorption onto soil minerals, complexation with small or large organic molecules in the soil, as well as chemical precipitation into insoluble forms.

SITES AND SOILS

The soils used in the laboratory studies were obtained from two operating HWLT sites, one closed land treatment site and a site which had soil contaminated with coal tar. The soils were obtained from: (a) the Conoco, Ponca City, Oklahoma, closed oil refinery research land treatment site, (b) the Texaco, Anacortes, Washington, operating HWLT site; (c) a HWLT facility at a wood treating site (WTS) in Montana; and (d) a Niagara Mohawk Power Corporation (NMPC) site in New York. The Texaco (Anacortes) and the wood treating site in Montana have been authorized by the Environmental Protection Agency (EPA) as HWLT demonstration sites. These sites are being used to identify whether the wastes applied could be land treated to acceptable levels and to identify the optimal operational conditions for such treatment.

Two types of samples were obtained from the Texaco and the Conoco sites: (a) surface ZOI samples for a study to evaluate the spatial distribution of samples at such sites and (b) soil core samples taken as a function of depth to determine whether the wastes which had been applied to the surface had migrated. Only core samples were taken from the other two sites. The core samples were obtained from six depths (Table 3.1) from the surface.

TABLE 3.1 SOIL SAMPLES WERE TAKEN OF THE FOLLOWING DEPTHS AT THE RESPECTIVE SITES

0" - 6"	24" - 36"
6" - 12"	36" - 54"
12" - 24"	54" - 72"

The soil samples were collected at each site by personnel associated with Remediation Technologies, Inc. (ReTeC), Kent, Washington, placed in clean glass jars, labelled, transported immediately in cooler chests and stored in a 4°C room of the Environmental Engineering Laboratories at The University of Texas at Austin, until they were used. Approximately five kilograms of soil were collected at each location.

The following sections provide detailed descriptions of the sites: diagrams of the test plots, waste characteristics, climatological data and background soils information.

Texaco

Site Description – This land treatment site is located at the Texaco Puget Sound refinery in Anacortes, Washington. Information about the site was obtained from the Texaco Part B land treatment permit application(7) and from Texaco personnel. Land treatment at this site started in 1958. The east HWLT area (site from which the samples were collected) has received wastes since that date. A wide range of wastes, both hazardous and non-hazardous, were applied on an irregular basis since 1958 (Table 3.2). More complete records of applications started in 1980. Prior to that time, little information was available on the wastes that were applied. Plant personnel indicated that the earlier waste applications were of the same general type as that applied after 1980.

The type of waste, the frequencies of application, and the waste quantities applied all varied over time. Waste application records were available for many of the latter years for which the east HWLT plots were in operation. The quantity of wastes applied to the east plots, in terms of tons of oil applied per acre, during the period of 1980-1986 is indicated in Table 3.3. The total amount of waste applied to the site since it first began operation, and the specific waste constituents that were applied, are unknown.

TABLE 3.2 WASTES THAT HAVE BEEN PLACED ON THE TEXACO, ANACORTES HWLT UNIT(7)

Slop Oil Emulsion Solids (K049)
API Separator Sludge (K051)
Leaded Tank Bottom Wastes (K052)
Refinery Oily Waste (D001)
Refinery Scale (D001)
Surge Basin Sludge
Tank Sludge
Acid Spill Dirt
Cooling Tower Sludge
Texaco Minnesota Sludge
Minas Oil Spill Crude and Dirt
FCCU Catalyst
BDU Exchanger Sludge
BDU Asphalt
Alky Contactor Sludge
Clay Filter
Poly Catalyst
Seattle Terminal Sludge
Chromate Spill
Oily Dirt
Oily Water Sewer Sludge

In 1987, an evaluation of the physical status of the HWLT soils was conducted using 20 test pits that extended about 12 feet from the surface. The evaluation(7) established that as the waste applications and incorporations were made over time,

TABLE 3.3 TONS OF OIL APPLIED TO THE EAST HWLT PLOTS AT THE TEXACO, ANACORTES HWLT UNIT--1980-1986(7)

Plot	Total Tons of Oil Applied per Acre
1	74
2	112
3	114
4	57
5	36
6E	174
6EC	235
6WC	355
6W	369

the surface of the plots rose due to the amount of contaminated soil and sludge that was applied and to the treated waste residuals that accumulated. The original base of the treatment zone in each plot remained stationary. Over the east HWLT unit, the treated waste residual thickness averaged about 26 inches (0.66 m) with a range of 18 to 42 inches (0.45 to 1.1 m).

The samples taken for this study were from an area where the accumulated treated waste residuals appeared to have raised the surface by about 30 inches (0.76 m). The soil depths noted in this report for the Texaco samples are from the surface of the plot as it existed at the time of sampling.

The total area of the Texaco east HWLT site is 7.34 acres in size with nine separate management areas. The area from which the samples were taken for this study was a plot approximately 63 feet by 460 feet (19 m by 140 m). The locations of the depth samples are noted in Figure 3.2. Samples were collected from three separate locations (labelled A, B, and C in one test plot) at about 120 foot (36 m) intervals from south to north. Including the duplicate samples, a total of 12 samples were taken from each test pit. The sites marked with numbered solid dots indicate the locations of the ZOI samples used in the separate spatial distribution study (Section 6). The area is now used only for the treatment of EPA hazardous wastes listed as K049, K051, and K052. Average annual precipitation in this area is 27 inches per year. Mean annual temperature is 51°F.

Background and HWLT Soils Data – Information about the characteristics of the background soils and the HWLT soils was available in the Part B land treatment permit application(7). These characteristics represent those noted at the site in evaluations conducted before the soil samples for this study were obtained. No background soils data were obtained as part of this study.

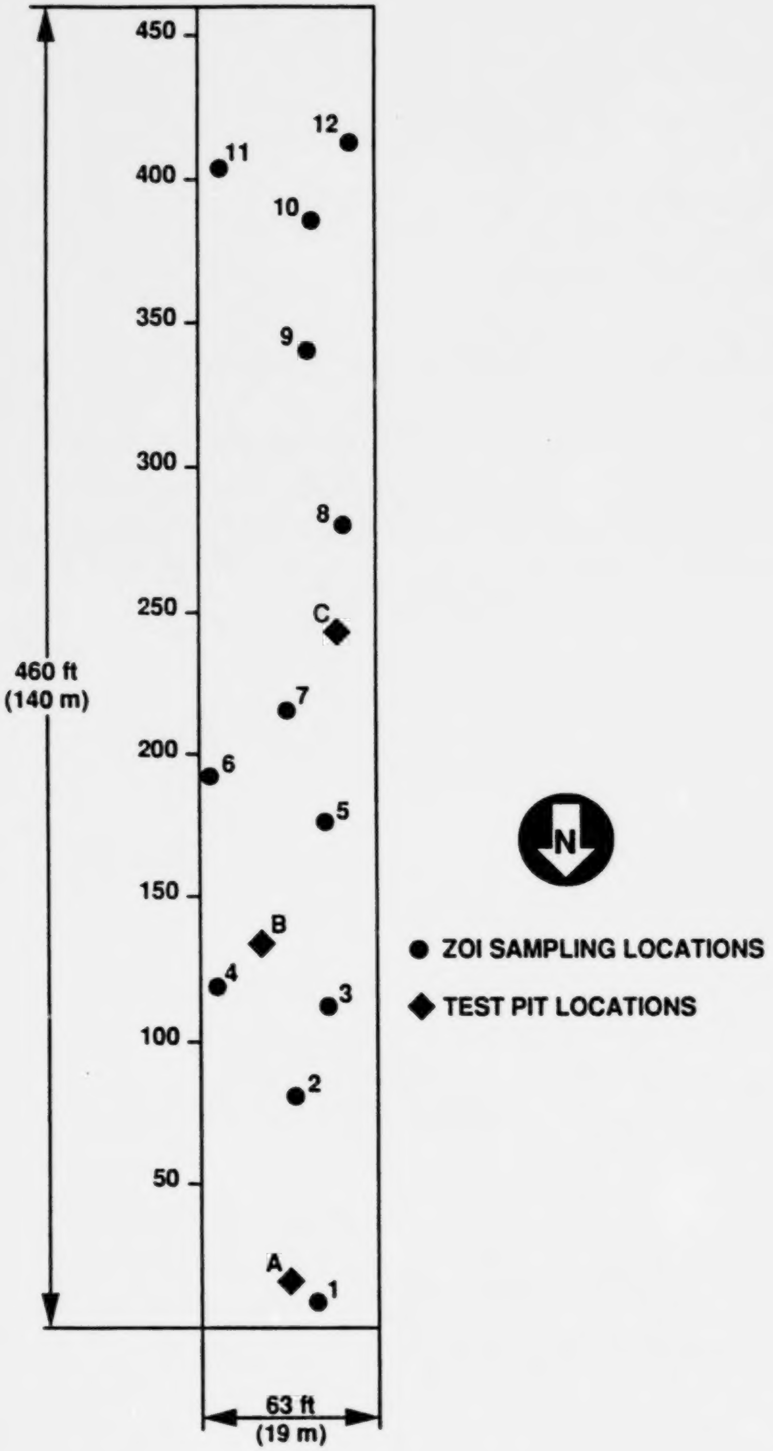
450
400
350
300
250
200
150
100
50
460 ft
(140 m)
63 ft
(19 m)
1
2
3
4
5
6
7
8
9
10
11
12
A
B
C
N
● ZOI SAMPLING LOCATIONS
◆ TEST PIT LOCATIONS

FIGURE 3.2 TEXACO ANACORTES SAMPLING LOCATIONS

i) Background Soils – As noted in the Part B application, the background soil samples for the 1985 study were taken from areas immediately adjacent to but outside of the HWLT plots. Four soil cores were obtained from two background areas for a total of eight cores. These cores were sampled to a depth of 10 feet (305 cm) and samples from the following intervals were evaluated (0-15, 15-45, 45-90, 90-150, 150-200, 200-250 and 250-305 cm). Background soil samples also were obtained for separate 1984, 1986 and 1987 studies described in the Part B application(7). The exact location of these background samples was not clearly identified in the information provided. It was assumed that the other background samples were obtained from a similar or the same location as the background samples for the 1985 study.

Analysis of samples taken in 1986 indicated an oil and grease content ranging from non-detectable to 0.04% in site background soils. The concentrations of volatile and acid extractable organics in background soil samples analyzed in 1986 were non-detectable or very low (Table 3.4).

TABLE 3.4 CONCENTRATION (mg/kg)+ OF VOLATILE AND ACID EXTRACTABLE ORGANICS IN BACKGROUND SOILS AT THE TEXACO, ANACORTES LAND TREATMENT SITE(7)

Chemical	Depth (feet)++ 0-1	5-6	Detection Limit
Benzene	ND*	ND	0.01
Toluene	ND	ND - 0.02	0.01
Ethylbenzene	ND	ND	0.01
Xylenes	ND	ND	0.01
σ-Cresols	ND	ND	0.08
m,p-Cresols	ND	ND - 1.19	0.08

+ *range of concentrations from samples taken at four background locations, 1986 study*

++ *1 ft = 30 cm; 5 ft = 150 cm; 6 ft = 180 cm*

* *not detected*

The average metal concentrations in site background soils are noted in Table 3.5. The agronomic and related parameters in these soils are presented in Table 3.6. The background soils were noted as a loamy sand with an acid pH and with a low organic carbon (TOC) content at the lower depths. In 1986, EP toxicity measurements

TABLE 3.5 AVERAGE+ TOTAL METAL CONCENTRATIONS (mg/kg) IN SOILS AT THE TEXACO, ANACORTES LAND TREATMENT SITE(7)

Depth from Surface (feet)++	Metal						
	As	Cr	Co	Pb	Hg	Ni	V
Background Soils*							
0-1	6.7	28	12	8	ND*	30	70
3-4	7.3	38	13	10	ND	33	57
4-5	7.4	39	13	10	ND	35	59
5-6	7.6	39	17	ND	ND	43	65
Hazardous Waste Plots (East Plots)							
0-1	6.3	286	31	72	0.8	338	223
3-4	6.8	39	14	ND	ND	39	62
4-5	7.5	38	15	ND	ND	39	64
5-6	7.3	39	15	ND	ND	42	67

+ *averages of data from 1985, 1986 and 1987 studies*

++ *1 ft = 30 cm; 3 ft = 90 cm; 4 ft = 120 cm; 5 ft = 150 cm; 6 ft = 180 cm*

* *data not available for the 1-3 ft interval*

TABLE 3.6 AGRONOMIC PARAMETERS IN SOILS AT THE TEXACO, ANACORTES LAND TREATMENT SITE – 1985 STUDY(7)

Depth (ft)*	pH	Total Salts (meq/L)	Nitrogen (mg/kg)	Total P (mg/kg)	CEC (meq/100 gm)	TOC (%)
Background Soils+						
1.5	5.5	5.6	908	254	12.6	1.64
5	6.2	2.8	288	287	16.9	0.39
6.5	6.8	2.1	155	164	18.4	0.17
10	7.0	2.0	160	190	18.5	0.15
Hazardous Waste Plots++						
1.5	6.4	22.8	1535	754	26.6	7.00
5	6.4	5.8	370	192	14.8	1.32
6.5	7.0	4.0	145	252	18.5	0.14
10	7.3	4.8	145	274	18.7	0.13

* *1.5 ft = 45 cm; 5 ft = 150 cm; 6.5 ft = 200 cm; 10 ft = 305 cm*

+ *mean values of two samples at each depth*

++ *mean values of six samples at each depth* were made for Cr, Pb, Ni and V in extracts of samples of background soils. The concentrations of these metals in the EP extract in the 0-1 and 5-6 feet depth samples were below the detection limit of 0.1 mg/L.

ii) HWLT Soils – Several evaluations of the organics and metals in the ZOI and the LTZ of the HWLT plots were conducted during the period of 1983 to 1988(7). In a 1984 study, the total PAH content in the ZOI of the east and west HWLT plots averaged 1.52% and 1.38%, respectively. The oil and grease content of the ZOI soils in the east and west HWLT plots averaged 6.85% and 7.48%, respectively. These values are considerably greater than for the background soils and are one measure of the waste residue accumulation that has occurred.

In 1985, volatile, acid extractable, and base neutral extractable organics were measured in the ZOI and LTZ soils. No acid extractable organics were found. The only volatile organic detected was 1,4-dioxane at 530 ug/kg in one ZOI sample (0-45 cm). Quantification of this compound at the detected level in only one sample was not considered significant.

A number of PAH compounds were found in the HWLT soils in the 1985 study (Table 3.7). Except for chrysene and pyrene, these compounds were not found at above detection limits in all of the samples analyzed.

TABLE 3.7 BASE NEUTRAL EXTRACTABLE FRACTION (PAH) COMPOUNDS DETECTED IN ZOI AND LTZ SOILS AT THE TEXACO, ANACORTES HWLT SITE – 1985 STUDY(7)

Compound	Depth of Sample (cm)[+]	Concentration Range (ug/kg) (measured/detection limit)	Measured in Following Samples[++]	Total Samples Analyzed
Benz(a)anthracene	0-45	3200/1600 to 21,000/5000	5	9
	45-150	1200/320 to 7300/1100	4	9
Benzo(b)fluoranthene	0-45	4600/3000 to 14,000/1600	2	9
	45-150	8500/510	1	9
Benzo(a)pyrene	0-45	3300/2200 to 59,000/1600	3	9
	45-150	420/320 to 43,000/510	2	9
Chrysene	0-45	4000/1000 to 75,000/5000	9	9
	45-150	3700/320 to 15,000/1100	9	9
	150-200	1800/640	1	9
	200-305	1600/320	1	9
Fluoranthene	0-45	6700/3000	1	9
	45-150	440/320 to 2600/1100	3	9
1-Methyl Naphthalene	0-45	3900/2200	1	9
	45-150	1200/320 to 1300/640	2	9
Phenanthrene	0-45	7000/2200	1	9
	45-150	750/320 to 1700/640	4	9
Pyrene	0-45	3100/1600 to 41,000/5000	6	9
	45-150	590/640 to 17,000/1100	9	9
	150-200	450/320 to 950/640	2	9

[+] *45 cm = 1.5 ft; 150 cm = 5 ft*

[++] *samples in which the compound was found at concentrations above detection limits*

Another evaluation of the Anacortes HWLT site was undertaken in 1987. At that time, the concentrations of volatile organics and of base neutrals in background soils and soils in specific HWLT plots were determined. No volatile organics and only one base neutral, benzo(a)fluoranthene at 740 ppb in the 0-1 ft sample, were found in background soils. In addition, the volatile organics and base neutrals that were found in the HWLT soils were found in the samples taken from the top one foot. Table 3.8 presents the concentration of these compounds that were found in the samples from the four east HWLT plots that were evaluated in the 1987 study. These data are similar to the 1985 data and also indicate that the accumulated PAH compounds were being retained in the surface soils.

TABLE 3.8 VOLATILE ORGANICS AND BASE NEUTRALS IN SOILS FROM THE EAST HWLT PLOTS⁺ – TEXACO, ANACORTES – 1987 STUDY(7)

	Depth Below Ground Surface (ft)			
Chemical	**0-1**	**5-6**	**6-7**	**7-8**
Volatile Organics (ug/kg dry basis)				
Benzene	ND⁺⁺	ND	ND	ND
1,4-Dioxane	ND	ND	ND	ND
Styrene	ND	ND	ND	ND
Ethylbenzene	ND	ND	ND	ND
Toluene	ND-180	ND	ND	ND
o-xylene	ND	ND	ND	ND
m- & p-xylene	ND	ND	ND	ND
Pyridine	ND	ND	ND	ND
Base Neutrals (ug/kg dry basis)				
Naphthalene	ND	ND	ND	ND
1-Methyl Naphthalene	ND-120	ND	ND	ND
Phenanthrene	ND-150	ND	ND	ND
Anthracene	ND	ND	ND	ND
Fluoranthene	ND	ND-97	ND	ND
Pyrene	300-96,000	ND-59	ND	ND
Chrysene	1100-220,000	ND	ND	ND
Benzo(a)anthracene	350-88,000	ND	ND	ND
Benzo(a)pyrene	2000-61,000	ND	ND	ND
Benzo(a)fluoranthene	31,000-52,000	ND	ND	ND

⁺ *range of concentrations found in the four East HWLT plots that were sampled: plots 3, 6E, 6WC and 6W*

⁺⁺ *detection limits were 3 ppb for all volatiles except 1,4-Dioxane and pyridine; 150 ppb for 1,4-Dioxane and pyridine; and 50 ppb for the base neutrals*

The average metal concentrations as a function of depth in the east HWLT plots were determined and were presented in Table 3.5. The surface soils had higher Cr, Co, Pb, Hg, Ni and V concentrations than the background soils. However, the concentrations at the lower depths were comparable to background soil concentrations. In 1986, the EP procedure was used to determine the concentrations of Cr, Pb, Ni and V in extracts of 0-1 ft and 5-6 ft depth soil samples from the east HWLT plots. None of the 15 samples from throughout the plots had extract concentrations of these metals above the detection limit of 0.1 mg/L. The summary of the previous data(7) concluded that the metals were being immobilized within the treatment zone and remained within the surface soils with no metals migration below the original ZOI of the site.

The agronomic parameters measured in the east HWLT plots were presented in Table 3.6. The data indicated that the application of the petroleum industry wastes to the site increased the total salts, pH, nitrogen, total phosphorus, CEC and TOC of the surface soils over that of the background soils. At greater depths, the concentration of these parameters were comparable to background soils. The total salt concentration in the soils was greater than background at all depths.

The treatment zone soil pH was within the optimum range for waste treatment and immobilization for metals and appeared to be stable. No applications of lime were used to maintain the soil pH during the active operation of the facility.

The HWLT soils had a CEC in the 15-30 meq/100g range with calcium and magnesium being the dominant cations found on the exchange sites. The treatment zone soils were characterized as having a high base saturation. The soil nutrient levels in the ZOI were within a reasonable range for waste treatment.

Conoco

The information in this section was provided by Conoco personnel who were involved in the prior use of this site. The research site at the Conoco, Ponca City, Oklahoma, facility consists of 27 plots, each approximately 20 feet by 25 feet (6 m by 7.6 m). A key objective of prior research conducted at this site was to assess the rate of oil degradation. Twenty-seven plots were established and eighteen plots received oily wastes. The other 9 served as controls. Wastes were applied in 1976, 1978 and 1979. One set of plots received a total of 5% (oil-in-soil weight percent) waste as a loading rate, another set received a total of 10%, and the final set received a total of 15%.

A description of the research site and the results that were obtained is available(8). The following provides background information on the site and its use.

Prior to application of wastes, the test plots were prepared by diking, tilling liming and fertilizing. Tilling was done with a tractor-pulled rotary tiller. Lime was added to the plots at the rate of 6.2 tons per acre (68% $CaCO_3$ equivalent). Fertilizer was added at two rates: 11.5 or 23 pounds of ammonium nitrate per plot plus 3 pounds of triple superphosphate per plot (equivalent to 110 or 220 pounds of nitrogen per acre plus 40 pounds of P_2O_5 per acre).

Waste was first applied to test plots in May 1976. Wastes were applied over all three sections of each test plot at a rate sufficient to provide approximately 5 weight percent oil-in-soil when mixed into the top 6 inches of soil. These wastes were allowed to dry for about 5 weeks and were then rototilled into the top 6 inches. One year later, some of the test plots received waste to bring the total amount of oil loaded up to 10 weight percent on those sections. In the spring of 1978, some test plots received a third 5 weight percent oil-in-soil waste addition. All waste additions occurred by covering the diked plots with waste pumped from a vacuum truck. The wastes were allowed to dry for a period of time (approximately 4 to 6 weeks) before being tilled into the top 6 inches of soil.

For this study, test pits for sampling at the required depths were trenched approximately 4 feet wide by 8 feet long (1.2 m by 2.4 m), with samples taken from three sides (labelled A, B, and C) of the trench as shown in Figure 3.3. Only one test pit was used because the sample plots were too small for triplicate test pits. Samples were obtained in duplicate at each of the six depths noted in Table 3.1. The locations of the test pits and of the ZOI samples taken for use in the spatial variability study (Chapter 6) are shown in Figure 3.4.

The types of waste applied to the research plots are noted in Table 3.9. These wastes were applied to the soil as they were generated, with no segregation by waste type. The amount indicated in Table 3.9 represents the total amount of waste applied to the test plots, not the amounts applied to each plot.

Since the research studies ceased in 1979, no further waste applications have occurred. The site has received periodic tilling. Annual rainfall in the Ponca City area is 34 inches and the mean annual temperature is 61° F

Data on the soils at the Conoco, Ponca City land treatment site were collected in 1976 before wastes were applied. The background soils were classified as a silt loam at the surface and a silty clay loam at depths to 150 cm. The characteristics of these soils are noted in Tables 3.10 and 3.11. Other background data collected at a later date in support of a land treatment permit application are presented in Table 3.12.

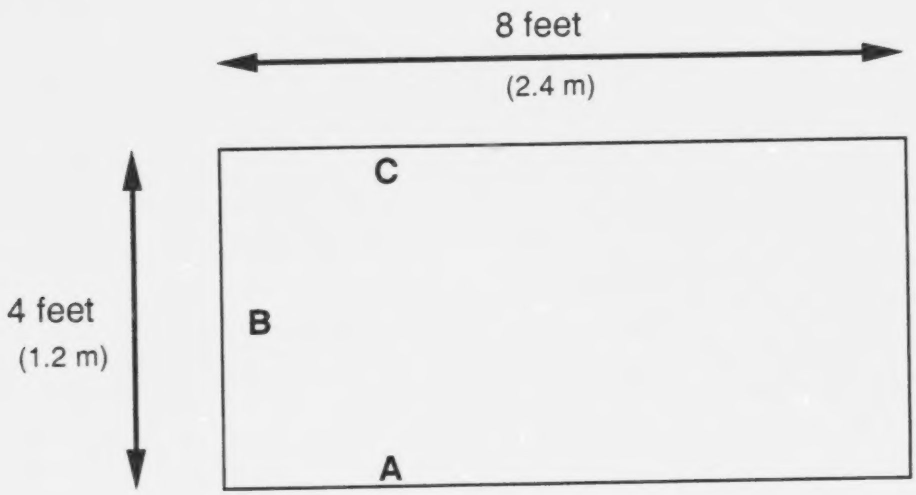

FIGURE 3.3 TOP VIEW OF A CONOCO SAMPLING TEST PIT

TABLE 3.9 AMOUNT OF WASTE APPLIED+ TO THE CONOCO RESEARCH SITE

Waste Type	Wet Tons
API Separator Bottoms	900
Wastewater Treatment Unit Sludges	700
Slop Oil Emulsion Solids	400
Coker Blowdown Pond Sludges	300
Weathered Leaded Tank Bottoms	2,000
Non-leaded Tank Bottoms	400

+ *during three years of operation – 1976, 1977, 1978*

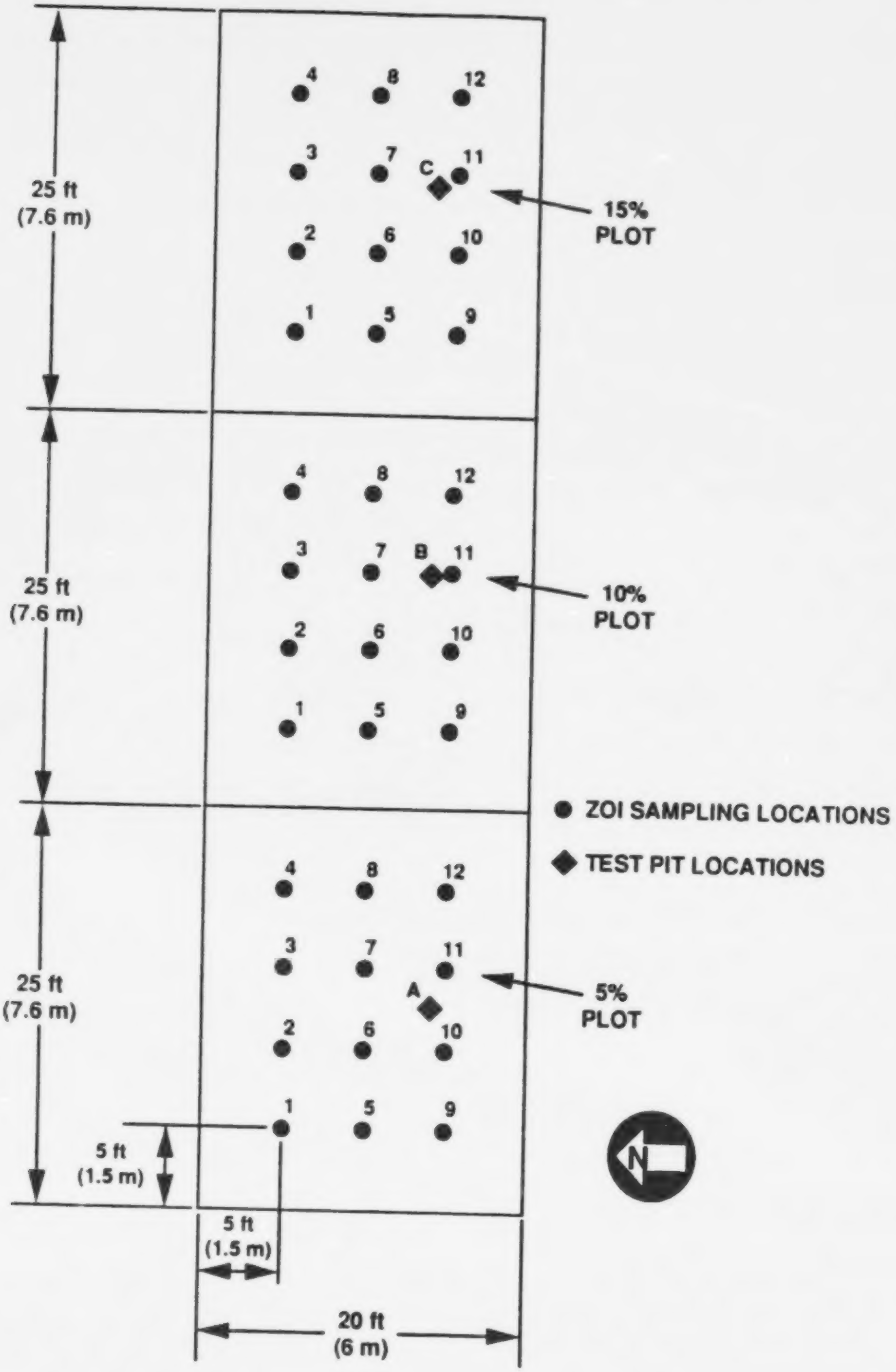
4
8
12
3
7
C
11
25 ft
(7.6 m)
15%
PLOT
2
6
10
1
5
9
4
8
12
3
7
B
11
25 ft
(7.6 m)
10%
PLOT
2
6
10
1
5
9
● ZOI SAMPLING LOCATIONS
◆ TEST PIT LOCATIONS
4
8
12
3
7
11
25 ft
(7.6 m)
A
5%
PLOT
2
6
10
1
5
9
5 ft
(1.5 m)
N
5 ft
(1.5 m)
20 ft
(6 m)

FIGURE 3.4 CONOCO PONCA CITY RESEARCH SITE SAMPLING LOCATIONS

TABLE 3.10 AVERAGE BACKGROUND SOIL CHARACTERISTICS – CONOCO, PONCA CITY LAND TREATMENT SITE – 1976 DATA

Sample Depth (inches)	pH	Organic Carbon (%)	Extractable Hydrocarbon (%)	CEC (meq/100 g)
0-6	4.9-6.0	1.10	0.032	10.5
6-12	5.3-5.4	0.90	0.018	8.5-10.8
12-18	5.7-6.7	0.77	0.013	15.2
18-24	5.9-6.7	0.67	0.013	13.0-14.9
24-36	6.3-6.7	0.51	0.009	–
36-48	6.5	0.44	0.012	–
48-60	–	0.27	0.006	–
60-72	–	0.19	0.003	–

TABLE 3.12 BACKGROUND SURFACE AND SUBSURFACE SOIL CHARACTERISTICS+- CONOCO, PONCA CITY LAND TREATMENT SITE – 1984 DATA

Parameter	Surface soil (0-15 cm depth)	Subsurface Soil (30-45 cm depth)
Porosity (%)	48.7	46.2
CEC (meq/100 g)	18.6	25.1
Bulk Density (gm/cc)	1.39	1.46
pH	5.6	6.1
Phosphorus (ppm as P)	9	8
Potassium (ppm as K)	94	83
Calcium (ppm as Ca)	1110	1100
Magnesium (ppm as Mg)	191	311
Sodium (ppm as Na)	69	89
Electrical Conductivity (μ mhos/cm)	0.4	0.5
Total Organic Carbon (%)	2.4	2.1
Total Nitrogen (%)	0.13	0.09
Oil and Grease (mg/kg)	157	97

+ *average of four samples*

TABLE 3.11 AVERAGE[+] METAL CONCENTRATIONS (mg/kg) IN BACKGROUND SOILS – CONOCO, PONCA CITY LAND TREATMENT SITE – 1976 DATA

Sample Depth (inches)	Al	Ba	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Ti	Zn
0-12	46	500	2400	<2	18	12	19,000	3700	520	6500	19	20	4400	45
12-18	57	540	2600	<2	20	15	27,000	4000	560	5100	23	23	4200	54
24-36	63	–	3350	–	–	–	23,500	5100	600	4700	–	–	5300	–
36-48	48	–	2400	–	–	–	20,000	4100	540	4800	–	–	5000	–
60-72	40	–	3200	–	–	–	20,000	4200	450	4900	–	–	4800	–

[+] *number of samples analyzed varied with depth: n = 9 to 11 for the 0-12" and 12-18" samples, and 1 to 5 for other samples*

Wood Treating Site

This site did not meet all of the extended period of time criteria for this project (Section 1). It was included because it was an active land treatment effort with K-001 wastes for which information on site conditions, waste characteristics and site operation was available. Thus, the results from this site were not expected to be comparable to those from the Texaco and Conoco sites where wastes had existed for over ten years.

This site is located in Montana. Information about this site was provided by ReTeC personnel based upon their involvement in the activities at this site. Two separate test plots were established in 1985 as a Land Treatment Demonstration (LTD) site. The waste applied at this LTD site was the sludge (settled material) from an impoundment that was used for the disposal of creosote contaminated waste waters from a former railroad tie treating operation. The sludges were a black, oily cake-like material that contained a significant amount of soil and vegetation debris. Prior to this study, samples of this material were sampled for metals and base neutral compounds. This sludge had low metal concentrations and high PAH concentrations (Table 3.13).

The LTD plot from which the core soil samples were obtained was operated in the following manner. Sludge was initially added to the plot in an amount (about 4 inches) to result in about 4% benzene extractables in the ZOI. Ten weeks after startup, the sludge was reapplied to the plot to achieve an additional 4% benzene extractables in the soil. The soil pH was maintained near neutral and the plot was tilled bi-weekly to aerate and mix the top 6-12 inches of applied sludge and soil.

The soil samples for this study were taken about one year after the LTD study was completed. Figure 3.5 indicates the dimensions of the LTD plot and the location of the test pits used to obtain samples for this study. Soil samples were taken in duplicate at each of the six depths noted in Table 3.1.

Average yearly precipitation for this area is 23 inches, approximately evenly distributed over the entire year. Mean temperature in this area is 47° F.

The soils at this site are composed of a fine sandy loam which grades with depth to a fine sand at approximately three feet. Gravel with occasional cobbles was observed below the treatment zone in one of the test pits. The soil parent material is alluvium. The mineralogy of these soils is mixed in that no specific type of clay mineral (kaolinite, illite, or montmorillonite) dominates. The topography of the immediate area is nearly level with less than two percent slope. The soils are well drained and have only a slight to no erosion hazard. The permeabilities are moderate at the surface changing to moderately rapid at depths ranging from 40 to 70 inches when the sand/gravel layer is encountered.

In 1985 and prior to this study, sixteen surface soil samples (0-1 ft) from over the entire site were taken to characterize the basic site chemical properties prior to use. The results are presented in Table 3.14. The bulk density of these soils ranged from 1.3 to 1.5 grams/cubic centimeter which are typical values for agricultural soils. Soils with these bulk densities tend to have very good aeration characteristics which allow the free movement of oxygen and carbon dioxide into and out of the soil. The porosity values ranged from 43 to 51%. These soils had an acidic pH and a low electrical conductivity and salt content.

No other data was available on the background characteristics of the soil at the LTD site. However, some data was available on the characteristics of sub-surface soils at a site about 0.5 to 0.75 mile from the LTD site. The available data is presented in Table 3.15. Based on soil survey information, the soil series in the area are fairly constant.

TABLE 3.13 CONCENTRATIONS OF METALS AND BASE NEUTRAL COMPOUNDS IN THE K-001 SLUDGE APPLIED TO THE WOOD TREATING SITE LTD PLOT

Chemical	Concentration (mg/kg)
Metals	
Arsenic	<1.5 - 7.0
Barium	<140
Cadmium	<15
Chromium	<15
Copper	22 - 35
Lead	<29
Mercury	<0.2 - 0.3
Nickel	28 - 53
Zinc	28 - 130
Base Neutral Compounds	
Naphthalene	5,190 - 14,200
1-Methyl Naphthalene	1,750 - 4,550
2-Methyl Naphthalene	1,000 - 2,430
Diethyl Naphthalene	910 - 1,290
Dimethyl Naphthalene	1,490 - 2,220
Acenaphthene	7,410 - 19,800
Fluorene	8,670 - 18,600
Phenanthrene	17,700 - 41,830
Methyl Phenanthrene	3,120 - 4,790
Pyrene	10,300 - 22,900
Fluoranthene	10,800 - 25,100
Benzo(a)anthracene	2,390 - 4,110
Benzo(a)pyrene	365 - 2,400
Benzofluoranthene	550 - 2,030

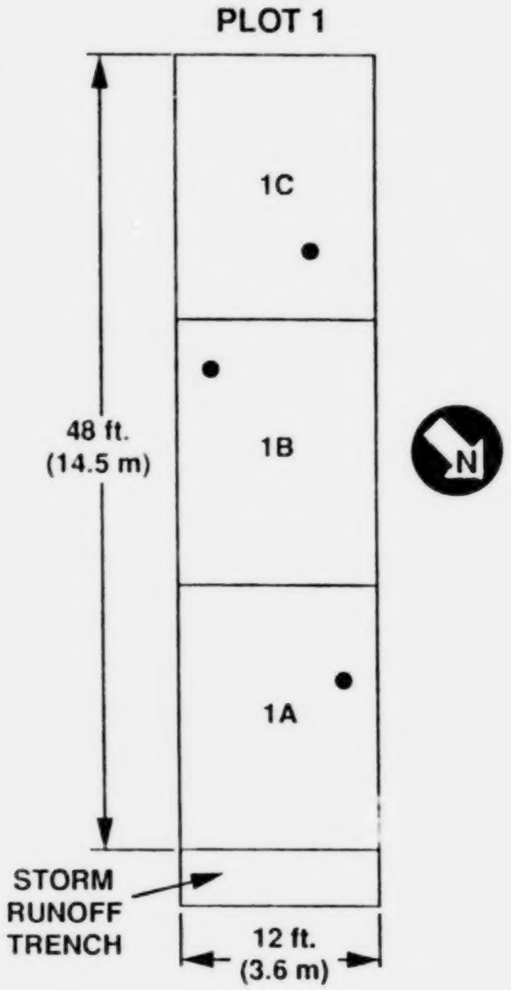
PLOT 1
1C
1B
1A
48 ft.
(14.5 m)
N
STORM
RUNOFF
TRENCH
12 ft.
(3.6 m)

FIGURE 3.5 WOOD TREATING SITE TEST PIT SAMPLING LOCATIONS

TABLE 3.14 AVERAGE+ BACKGROUND ZOI CHARACTERISTICS – WOOD TREATING SITE – 1985 DATA

Parameter	Value
Bulk Density (gram/cm^3)	1.4
pH	6.4
Electrical Conductivity (μ mhos/cm)	0.73
CEC (meq/100 g)	21.4
Total Organic Carbon (%)	1.38
Organic Matter (%)	2.4
Total Kjeldahl Nitrogen (mg/kg)	115
Total Phosphorus (mg/kg)	362
Total Potassium (%)	2.39

+ *average of 16 samples*

TABLE 3.15 METAL CONCENTRATIONS IN SUBSURFACE SOILS FROM AN AREA NEAR THE WTS SITE

Metal	Concentration (mg/kg)
Arsenic	below detection limit of 0.5 mg/kg throughout the depth
Lead	
– depth of 36-54"	ave = 6.6; range = 2.5 - 10.2 (n = 8)
– depth below 60"	ave = 6.2; range = 3.6 - 9.1 (n = 8)

Niagara Mohawk Power Corporation (NMPC)

As noted earlier (Section 1), this NMPC site was not a HWLT site and the results obtained from samples taken at this site should not be construed to represent conditions at a managed HWLT site. The NMPC soils used in this project came from a NMPC site in New York where residues from manufactured gas plant operations were disposed of in a shallow open trench. The constituents in these soils represent organics and inorganics from coal tars. The coal tar was produced by a local power company between 1850 and 1930. Coal tar is obtained by the distillation of bituminous coal, and contains a variety of organic and inorganic compounds(9).

The coal tar was found in a gas holder in the early 1960s and hauled to the current site where it was placed into a shallow trench, approximately thirty yards long, ten yards wide and five yards deep. An estimated 4,000 gallons of coal tar were placed into the trench and left unattended until recently. The soil samples were taken directly from the disposal trench. Figure 3.6 shows the approximate locations of the sites from which samples were taken and composited for use in this study. The site is now covered with grass. The area receives an annual average rainfall of approximately 35 inches and has a mean temperature of 48° F.

A hydrogeological study of the site indicated that the unsaturated zone consisted of fine to coarse sand with some silt. The depth to water table generally is between 6 to 10 feet. The saturated zone soils consist of sand with some silt. The first aquitard, a clayey silt layer, is encountered between 20 to 38 feet below the surface.

No data on the chemical characteristics of the background soils were available.

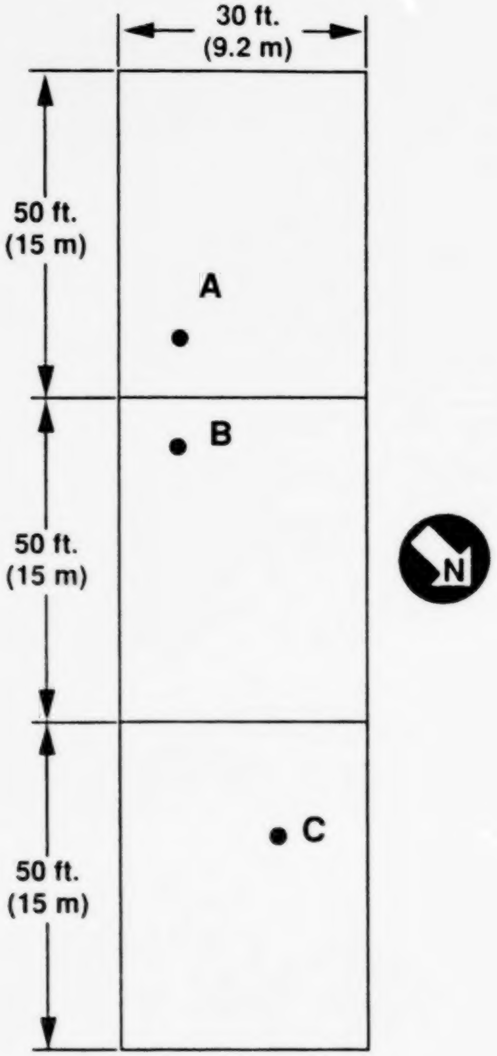
30 ft.
(9.2 m)
50 ft.
(15 m)
A
B
50 ft.
(15 m)
N
C
50 ft.
(15 m)

FIGURE 3.6 NIAGARA-MOHAWK TEST PIT SAMPLING LOCATIONS

SECTION 4

GENERAL MATERIALS AND METHODS

INTRODUCTION

This section identifies and describes the materials and methods that were used in many of these studies. Included are descriptions of: (a) the aerobic microcosm procedure that was used to determine chemical loss, (b) analytical procedures for inorganics, organics, and toxicity, and (c) the leaching procedure used to estimate relative mobility. Other methods used only in a particular aspect of the project are included in the Section describing that aspect.

MICROCOSM STUDIES

Biological degradation of organics in the soil is one of the most important mechanisms for their removal. The losses occur through a series of enzymatically catalyzed steps in which complex organic molecules are transformed into simpler organic or inorganic molecules. These biological reactions may be enhanced or retarded by environmental conditions. In this project, degradation studies were conducted by adding the test soil to glass beakers, also referred to as batch microcosms. These soils then were incubated and monitored for degradation (loss) of specific chemicals by testing for concentrations of the chemicals as a function of incubation time. Table 4.1 provides a general description of the aerobic batch microcosm protocol. For the anaerobic degradation studies, the aerobic microcosm procedure was modified and the anaerobic procedure is described in Table 4.2.

No abiotic controls were included in these studies. Available methods to kill microorganisms and cause abiotic conditions: (a) can cause changes in soil characteristics or chemical concentrations or (b) fail to maintain abiotic conditions over the lengthy period (many months) used in these microcosm studies. Therefore, in these studies, the exact mechanism of organic loss is unknown but was assumed to be due primarily to microbial degradation. However, for some compounds, such as naphthalene, loss due to volatilization also may have occurred.

TABLE 4.1 AEROBIC BATCH DEGRADATION RATE PROCEDURE

Each experiment consists of seven sample sets. Each sample set consists of four beakers (triplicates for a sample and one blank). The procedure for each experiment is as follows:

(a) Place 30-60 g of sample (contaminated soil), which has been kept at 4° C, into each 150 mL beaker and adjust the soil moisture content to 80% of field capacity with distilled deionized water. Place a glass stirrer in each beaker. Record all weights, including beaker, soil, water and glass stirrer.

(b) The sample beakers should be arranged so that any amendment is added to the day 0 sample last. For example, if the sample intervals are scheduled at day 1, 2, 4, 8, 16, 24, 32, the amendment is added to the sample sets for day 32, 24, 16, 8, 4, 2 and day 0 in that order.

Appropriate amendments also can be added to the contaminated soil prior to the mixture being placed in the beakers in step (a) above.

(c) During the study, check the moisture content in each beaker every week to keep it between 80% and 60% of the field capacity of the contaminated soil.

(d) Sacrifice sample sets at the selected time intervals for extraction, concentration and chemical analysis of specific chemicals.

(e) When experimental data verify that the chemicals of interest remaining in the soil are below the detection limit, the remaining beakers are discarded.

If uncontaminated soil is to be used in some of the experiments, such soil must be brought to test conditions prior to use. This is necessary to have the soil microorganisms acclimated to the test temperature and moisture content. The following will provide the desired acclimation.

(f) Place the uncontaminated soil, which has been kept at 4° C, in appropriate glass containers and adjust the soil moisture to 80% of field capacity with distilled deionized water.

(g) Mix soil and water thoroughly, cover the beakers with aluminum foil and place all the beakers in the dark at 20° C.

(h) Wait 10 days to allow soil microorganisms to equilibrate and become active.

(i) Mix the uncontaminated soil with the contaminated soil, and amendments as appropriate, and follow steps (a) through (e) above.

Because of resource constraints, only a subset of the organic compounds that could be in the soils were able to be evaluated. PAH were the specific organics evaluated because it is known that they degrade slowly over time, can accumulate at waste treatment and disposal sites, and are of concern to human health and the environment. The PAH compounds that routinely were monitored and their relevant characteristics are noted in Table 4.3.

TABLE 4.2 ANAEROBIC BATCH DEGRADATION RATE PROCEDURE

Each experiment consists of seven sample sets. Each sample set consists of four 125 mL serum vials (triplicates for a sample and one blank). The procedure for each experiment is as follows:

(a) Place 30-60 g of sample (contaminated soil), which has been kept at 4°C, into each 125 mL vial and adjust the soil moisture content to 75-80% of field capacity with distilled deionized water.

(b) Establish anaerobic conditions by introducing nitrogen into the vial at 450 mL/mm for 3.5 minutes. Immediately seal vial with a Teflon septa and crimp closure.

(c) Incubate all samples at 35°C.

(d) Sacrifice sample sets at the selected time intervals for extraction, concentration and chemical analysis.

(e) When experimental data verify that the chemicals of interest remaining in the soil are below the detection limit, the remaining vials are discarded.

TABLE 4.3 CHARACTERISTICS OF PAH COMPOUNDS MEASURED IN THIS STUDY(10)

	Aqueous Solubility µg/L @ 25° C	Molecular Weight
2-Ring		
naphthalene	31,000	128
3-Rings		
acenaphthylene	3930	152
acenaphthene	-	154
fluorene	1900	166
phenanthrene	-	178
anthracene	1290	178
4-Rings		
fluoranthene	265	202
pyrene	160	202
benzo(a)anthracene	10	228
chrysene	6	228
5-Rings		
benzo(b)fluoranthene	-	252
benzo(k)fluoranthene	-	252
benzo(a)pyrene	3	252
dibenzo(a,h)anthracene	-	278
6-Rings		
benzo(g, h, i)perylene	0.26	276
indeno(1, 2, 3-c, d)pyrene	-	276

ANALYTICAL PROCEDURES

The principal analytical procedures and instruments used were: (a) *organics* -- gas chromatograph (GC) and high pressure liquid chromatograph (HPLC), (b) *metals* -- flame atomic adsorption spectrophotometry, (c) *toxicity* -- Microtox© analyses, and (d) *mobility* -- Toxic Characteristic Leaching Procedure (TCLP). Freon extractables, volatile solids and moisture content of the soils were frequently measured.

GAS CHROMATOGRAPHY

Compounds extracted in methylene chloride were analyzed by capillary column gas chromatography. The analytical procedure followed is presented in EPA SW-846 (Method 8040)(11). The method consisted of injection of a 1 μL sample into a gas chromatograph (Hewlett Packard Model 5890A) which was equipped with an electronic integrator (Hewlett Packard Model 3392A), a capillary column, and a flame ionization detector. The chromatographic system was calibrated using an internal standard technique each day.

The operating conditions of the capillary column gas chromatograph are presented in Table 4.4. The initial temperature and temperature progress rate were selected based on the retention times of the test compounds and the internal standard. The initial oven temperature was 50°C and after an initial three minute delay was increased at a rate of 20°C/minute, to a final temperature of 270°C. A five-minute holding time was utilized at the termination of each run in order to ensure that the column was clean.

HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC)

HPLC analyses were used to quantify PAH in acetonitrile extracts of soil and aqueous samples. For analysis, 20 μL volumes of such samples were injected into the chromatograph using a Waters model 700 WISP automatic sampling device and pumped onto a Waters Radial Pak C-18 PAH Column using a linear solvent gradient (35:65::acetonitrile:water to 100% acetonitrile in 30 minutes) at a flow of 2.0 mL/min. Compounds eluted from the column were detected using a Waters 484 variable wavelength detector (254 nm) and subsequently integrated and processed by an NEC APC IV computer operating with Dynamic Solutions Maxima chromatography software. Duplicate samples were analyzed to monitor instrument accuracy.

Sample standards for the HPLC analyses were made using dilutions of a commercially prepared standard (Supelco 610-M PAH mixture). The stock was diluted

TABLE 4.4 OPERATING CONDITIONS FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF COMPOUNDS IN METHYLENE CHLORIDE

Condition		Description
Capillary Column		Supelco SPB-5 fused silica (dimensions: 30 m length x 0.53 mm I.D. x 0.5 μm film thickness)
Temperature	*During Run*	50°C for 3 minutes followed by increase of 20°C per minute to final temperature.
	Final	270°C at 5 minutes
	Injection Port	250°C
	Detector	300°C
Detector		Flame Ionization
	Hydrogen Gas Rate	30 mL/minute
	Air Rate	400 mL/minute
Carrier Gas	*Helium Rate*	20 mL/minute

in acetonitrile in volumetric flasks, and the dilutions were transferred to 10 mL vials and stored at -18° C until required for analysis. Standard solutions for each compound were run prior to sample analysis for external standard calibration.

FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

The metals of interest were: cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn). These metals were selected because: (a) Cd, Cr, Pb and Ni are hazardous constituents and are part of groundwater monitoring requirements, (b) Zn and Cu are relatively abundant in both native soils and in the wastes involved in this research, and are of interest to possible future crop production if the site is closed, and (c) these metals were expected to be present in the types of wastes applied to the test plots.

Prior to analyses, each sample was digested according to SW-846(11) Method 3010, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy." All digested samples were analyzed using a Perkin-Elmer 303 Flame Atomic Adsorption (FLAA) spectrophotometer. Four standards, previously calibrated and stored in acid solutions, were used for each metal calibration curve. Each standard was analyzed in triplicate. Each sample was analyzed at least twice and the average peak height used to determine the concentration of the sample.

The daily operating standards were prepared from laboratory grade 1000 ppm standards and diluted with ASTM Type II water to the appropriate concentrations. The standards were purchased from Fisher Scientific Company (Cu, Cr and Zn), Harleco (Pb and Cd), and Ricca Chemical Company (Ni). The standards were stored in solutions acidified with nitric acid to a pH of 2 to maintain the metals in solution at the correct concentrations.

MICROTOX ANALYSIS

The usual procedures to quantify the biological toxicity of a chemical are assays which measure the effect of a chemical on a test species under specified test conditions. Toxicity assays utilize a variety of test species that include rats, fish, invertebrates, microorganisms and plant seeds. Toxicity assays using bacteria as the test organism are gaining popularity due to their rapidity, ease in handling, cost effectiveness and the use of a statistically significant number of test organisms. The Microtox© assay is a microbial assay used for toxicity measurement, hazard assessment, and quantitative-structure activity relationship (QSAR) studies of environmental pollutants(12,13).

The Microtox© system is a relatively simple, rapid and inexpensive test and was used as the toxicity screening method in this project. The use of the Microtox© procedure to screen and predict the treatability potential of waste in soil has been evaluated and found to be satisfactory(14,15).

The Microtox© system is a standardized toxicity test system which utilizes marine luminescent bacteria (*Photobacterium phosphoreum*) as indicator organisms. Bioluminescence of this test organism depends on a complex chain of biochemical reactions involving the luciferin-luciferase system. Chemical inhibition of any of these reactions causes a reduction in bacterial luminescence. The Microtox© toxicity assessment considers the physiological effect of a toxicant, and not just mortality.

The system utilizes an instrumental approach in which the indicator organisms are handled as chemical reagents. Suspensions of about one million bioluminescent organisms are "challenged" by addition of serial dilutions of an aqueous sample. A temperature controlled photometric detector quantifies the light output in each suspension before and after sample addition. Reduction of light output reflects physiological inhibition which indicates presence of toxic constituents in the sample. The small sample volume required (~10 mL) is a positive aspect of the system.

The instrument used was the Beckman Microtox© Model 2055 Toxicity Analyzer System. Procedures indicated in the Microtox© System Operating Manual(16) were followed.

An EC_{50} value is the end point of interest using the Microtox© procedure. The EC_{50} is the concentration of a chemical that causes a 50% decrease of light produced by luminescent bacteria in the Microtox© test. The method provides for simultaneous testing of a control and an aqueous extract of a sample. The percent light decrease after 5 minutes is plotted against sample concentration. The concentration of toxicant that diminishes the light output by 50% is designated the EC_{50} under the defined conditions of exposure time and test temperature. When calculating EC_{50} values, responses for all concentrations are normalized against blank responses by multiplying the initial light output of each concentration by the mean blank ratio for time *t*. This normalization corrects for effects of light drift and offsets in light output due to dilution.

Low EC_{50} values indicate an extract or liquid sample with a greater toxicity potential and higher EC_{50} values indicate a low toxicity. Nontoxic samples will have an EC_{50} of around 100 (no decrease in luminescence) while toxic samples would have lesser values. EC_{50} values are useful as: (a) a relative screening evaluation for individual chemicals or combination of chemicals in water extracts to estimate relative toxicity, and (b) general input to decisions about waste or chemical concentrations that will be non-inhibitory to the soil microorganisms. The latter statement assumes that there is some relationship between Microtox© response and microbial activities in soil.

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The Toxicity Characteristic Leaching Procedure (TCLP) was developed to estimate the leachability of chemicals in a co-disposal land disposal facility, such as a landfill, that receives both municipal wastes and hazardous wastes. The TCLP was developed in three phases. Phase I consisted of extracting municipal waste with a leachate derived from municipal refuse using field lysimeters to collect municipal waste leachate (MWL) and a variety of laboratory media and contact procedures. This was to narrow the universe of potential candidate leaching procedures. Phases I and II are described in Kimmell and Friedman(17).

In Phase II, additional wastes were leached and the leachate procedure specifically defined. Two extraction fluids were identified for use, depending on the alkalinity of the solid phase of the waste. Alkaline soils (with a pH greater than 5.0, even after the addition of acid) require a fluid (Extraction Fluid #1) with a pH of 2.88 (±

0.05) made by adding glacial acetic acid to distilled water. Soils with a pH less than 5.0 require a fluid (Extraction Fluid #2) with a pH of 4.93 (± 0.05) made with acetic acid, sodium hydroxide and distilled water. The extraction time (18 hours) and the use of a Zero-Headspace Extraction Vessel for extracting volatiles also were established during this phase.

Phase III involved subjecting the draft TCLP to an evaluation of precision by the use of multi-laboratory collaborative studies. Results of such studies indicated that the TCLP was fairly reproducible by various laboratories and that the precision of the extraction had been increased over that of the prior method (EP Toxicity).

The TCLP, as proposed by EPA(18), was used in this research because of the increased reproducibility of the TCLP results as demonstrated by several researchers(19,20). The TCLP test also increases the probability for capturing organics, especially volatiles and semi-volatiles.

In the TCLP, partitioning is the major mechanism by which organic constituents are transported from the soil particles into the extraction fluid. An organic chemical is more likely to be partitioned into the extraction fluid when its organic carbon partition coefficient, K_{OC}, is low. When the K_{OC} is much greater than 1, the compound shows a preferential adsorption to organic matter over the extraction fluid.

Solubility is the determining factor of the transport of metals from the soil media to the extraction fluid during the TCLP. Solubility is affected by many factors, including pH, temperature, and oxidation state of the metal. The effects of pH are so significant on metal solubility that a different TCLP extraction fluid is used for two different soil pH ranges.

The basic procedure for one set of extractions (consisting of four soil samples) that was used is as follows. The pH of a 5.0 gram sample of the soil was determined by placing it in a beaker, adding 96.5 mL of distilled water, covering it with a watchglass, and stirring vigorously for five minutes using a magnetic stirrer. The pH was measured using an Orion digital Ionanalyzer Model 701 A. For samples with a pH of less than 5.0, Extraction Fluid #1 was used. Samples with a pH exceeding 5.0 require Extraction Fluid #2. All samples in this test required Extraction Fluid #1. Extraction Fluid #1 was prepared by adding 5.7 mL of glacial acetic acid to 500 mL of water, adding 64.3 mL of 1.0 N sodium hydroxide and diluting the solution to 1.0 L with double distilled water. The final pH was adjusted to 4.93 ± 0.05 with the addition of acetic acid or sodium hydroxide as necessary.

Twenty-five grams of soil were placed into the ZHE. Twigs, stones and roots were removed by passing the soil through a No. 9 sieve. Five hundred mL of

Extraction Fluid #1 were added to the vessel and the apparatus was sealed. Four vessels were placed onto the tumbler and rotated at approximately 30 rpm for 18 hours.

After the 18 hour agitation period, the vessels were removed from the tumbler and attached by a manifold system to a pressurized nitrogen tank. The vessels were connected to pre-weighed 500 mL glass storage bottles by Tygon tubing. The gas supplied pressure to the piston in the ZHE which, in turn, forced the extraction fluid through the filtration device at the top of the vessels. The vessels were subjected to pressure from the nitrogen in increments of 10 psi, allowing each vessel to stop dripping after each increment for at least 2 minutes before continuing on to the next pressure. All vessels were brought to a final pressure of 50 psi and held there until dripping had stopped for 2 minutes. The glass containers, now holding the filtered extraction fluid, were sealed, weighed and the weight recorded. These glass containers were then stored at 4°C until the extracts were analyzed for metals and organics.

FREON EXTRACTABLES

The soils also were analyzed for residual oil and grease as measured by the freon extractable procedure, SW-846(11), Method 9071, "Oil and Grease".

PERCENT MOISTURE

The percent moisture was determined gravimetrically by transferring a known weighed aliquot of the sample to a preweighed evaporating dish, evaporating to dryness at 103-105°C, and reweighing the dried solids. The loss of sample weight was reported as percent moisture(21).

VOLATILE SOLIDS

Volatile solids were determined by placing a previously dried sample in a tared crucible and igniting the sample at 550°C in a muffle furnace. The loss in weight upon ignition was reported as volatile solids(21).

SECTION 5

SITE SOIL-RESIDUE CHARACTERISTICS

As described in Section 3, the test sites received a variety of wastes over varying periods of time. Since application, the added wastes have undergone biological, chemical, and physical treatment in the soil and have been degraded, transformed or immobilized. The treatment processes that can achieve these changes in a soil are noted in Table 5.1.

TABLE 5.1 TREATMENT PROCESSES THAT CAN OCCUR IN SOIL

Adsorption	Flocculation
Aerobic biodegradation	Hydrolysis
Anaerobic biodegradation	Ion exchange
Chemical oxidation and reduction	Neutralization
Chemical precipitation	Volatilization
Detoxification	

The residues that have accumulated at these sites have increased the concentration of specific organics and inorganics in the soils. When discussing the contribution of an applied waste to the characteristics of a site soil, it is important to determine the background soil concentration of a chemical prior to any waste application. However, it was not within the scope of this project to obtain and analyze soil samples representative of background soils at each site. Data on many relevant parameters in background soils at the Texaco, Conoco and Wood Treating sites were available and were summarized in Section 3.

ORGANICS

Results from the Texaco site (Section 3) indicated that volatile and acid extractable compounds were not found in the HWLT soils but that PAH compounds were detected in concentrations considerably above background (Tables 3.7 and 3.8). In addition, PAH compounds are a common constituent of petroleum industry wastes, wood preserving wastes and coal tar. Thus, the soils from all four sites were evaluated for the sixteen PAH identified in Table 4.2.

Texaco (Anacortes) Site –

This site had detectable concentrations of most of all 16 PAH compounds in the top (0-6" and 12-24") soils of the site. The average concentrations of these compounds found at increasing depths from the current surface of the site are presented in Table 5.2. Figure 5.1 indicates the decrease in the concentrations of the three most prevalent compounds with depth at this site. As noted in Section 3, the application of wastes at this site has raised the topographic surface by as much as 30 inches. The dashed line in Figure 5.1 indicates the estimated location of the original surface of the site. The PAH concentrations in the top layers represent the accumulation of residues from the applied wastes. The absence of detectable concentrations of these compounds in the 36-54" layer indicates that these compounds had not migrated to this depth. Previous data (Tables 3.7 and 3.8) on the PAH compounds in the Texaco HWLT soils also indicated that the PAH concentrations decreased with depth and frequently were below detection limits at the lower depths.

The general trend of this data indicates that: (a) the PAH compounds have accumulated in the surface soils at this site, (b) the PAH concentrations decrease dramatically with depth and (c) some PAH compounds may be present at depths of 36-54" at this site. A more detailed sampling and analytical effort is needed to determine and verify that PAH compounds have migrated to such depths.

Freon extractable determinations also were done for the Anacortes test pit B samples. This analysis is a relative measure of the total oil and grease (O/G) residuals in a sample. The results are shown in Figure 5.2. The high levels of O/G in the top 24 inches of the profile again indicate the build-up of residuals at this site. The O/G concentration in the 0-6" samples was 61,700 mg/kg and was 56,600 mg/kg in the 6-12" sample. The O/G concentrations in soil samples taken below 24" were: 24"-36" – less than 1000 mg/kg; 36"-54" – 1680 mg/kg; and 54"-72" – less than 1000 mg/kg.

Conoco (Ponca City) Site --

The concentrations of PAH at this site were similar in type but much lower in concentration than those found at the Anacortes site. There has been no application of wastes at this site since 1978.

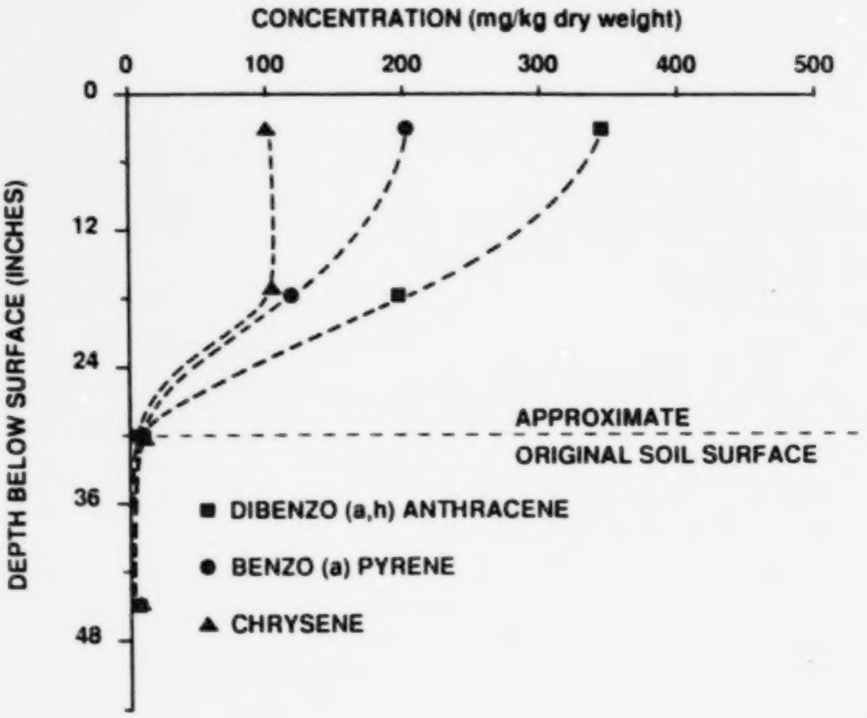

FIGURE 5.1 AVERAGE PAH CONCENTRATIONS AS A FUNCTION OF DEPTH-TEXACO, ANACORTES SOIL SAMPLES

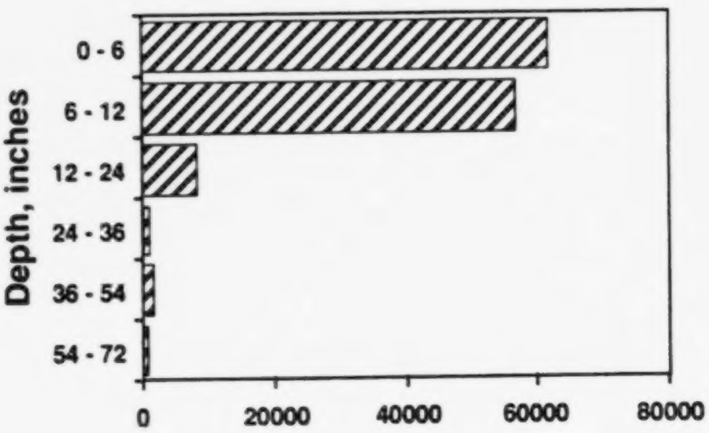

FIGURE 5.2 O/G (mg/kg) AS A FUNCTION OF DEPTH-ANACORTES TEST PIT B

O/G measurements were made on the samples from the 10% plot at this site. Only the top layer (0-6"), had a high concentration (5530 mg/kg). Below the six-inch depth, the O/G concentrations always were below the detection limits (1000 mg/kg) throughout the 72 inches sampled. The background O/G concentration of the surface and subsurface soils at this site were 157 and 97 mg/kg, respectively (Table 3.12).

TABLE 5.2 PAH CONCENTRATIONS* AT THE TEXACO SITE AS A FUNCTION OF DEPTH

Compound	Sample Depth**								Detection Limit+
	0-6"		12-24"		24-36"		36-54"		
	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Range	
naphthalene	1.8	1-2	2.8	2-5	1.5	<1-2.6	2.0	1.9-2.1	1.0
acenaphthalene	BDL	–	BDL	–	BDL	–	BDL	–	2.0
acenaphthene	BDL	–	BDL	–	BDL	–	BDL	–	1.0
fluorene	6.8	4-9	9.5	6-12	0.7	<0.2-2	BDL	–	0.2
phenanthrene	5.9	5-8	25	3-39	6.7	1-14	1.4	<0.1-3	0.1
anthracene	BDL	–	4.9	2-6	BDL	–	BDL	–	0.1
fluoranthene	30	26-38	75	19-100	BDL	–	BDL	–	0.2
pyrene	21	16-29	300	37-432	BDL	–	4.0	<0.1-7	0.1
benzo(a)anthracene	BDL	–	BDL	–	7.9	<0.1-20	BDL	–	0.1
chrysene	100	48-155	116	60-146	4.2	2-9	0.9	<0.1-2	0.1
benzo(b)fluoranthene	130	50-195	155	31-220	BDL	–	BDL	–	0.2
benzo(k)fluoranthene	BDL	–	BDL	–	BDL	–	BDL	–	0.1
benzo(a)pyrene	204	47-350	106	62-136	1.5	<0.1-3	BDL	–	0.1
dibenzo(a,h)anthracene	340	104-600	194	47-300	4.1	0.2-10	0.8	<0.2-2	0.2
benzo(g,h,i)perylene	82	25-160	51	8-85	BDL	–	BDL	–	0.2
indeno(1,2,3-c,d)pyrene	38	14-85	24	6-40	BDL	–	BDL	–	0.1

* *mg/kg dry weight of soil; average of samples from A, B and C pits (Figure 3.2)*

BDL *below detection limits*

** *samples from the 6" to 12" depth were not analyzed*

+ *detection limit of the analytical procedures used*

The PAH concentrations for the plot receiving the largest application (15% plot) as a function of depth are presented in Table 5.3. Below the ZOI, the PAH concentrations decrease with depth and fall below analytical detection limits. The same results were obtained for the 5% and 10% plots; that is, as in Table 5.3, there were very low to below detection limit concentrations at depths below 12 inches. A comparison of the average concentrations of PAH in the ZOI of the three Conoco plots is presented in Table 5.4.

TABLE 5.3 PAH CONCENTRATIONS* AT THE CONOCO SITE (15% Plot)

Compound	Sample Depth**								Detection Limit+
	0-6"		12-24"		24-36"		36-54"		
	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Range	
naphthalene	6.9	2-15	BDL	–	BDL	–	BDL	–	1.0
acenaphthalene	BDL	–	BDL	–	BDL	–	BDL	–	2.0
acenaphthene	16	12-18	BDL	–	BDL	–	BDL	–	1.0
fluorene	1.0	<0.2-1.5	BDL	–	BDL	–	BDL	–	0.2
phenanthrene	4.5	4-5	0.4	<0.1-1.1	BDL	–	BDL	–	0.1
anthracene	0.5	0.4-0.6	BDL	–	BDL	–	BDL	–	0.1
fluoranthene	BDL	–	BDL	–	BDL	–	BDL	–	0.2
pyrene	13	10-15	BDL	–	0.1	<0.1-0.2	BDL	–	0.1
benzo(a)anthracene	7.2	6.9-7.4	0.2	<0.1-0.6	BDL	–	BDL	–	0.1
chrysene	5.9	5-7	BDL	–	BDL	–	BDL	–	0.1
benzo(b)fluoranthene	5.1	4.3-5.6	BDL	–	BDL	–	BDL	–	0.2
benzo(k)fluoranthene	1.3	<0.1-4	BDL	–	BDL	–	BDL	–	0.1
benzo(a)pyrene	12	8-15	BDL	–	BDL	–	BDL	–	0.1
dibenzo(a,h)anthracene	37	29-41	BDL	–	BDL	–	BDL	–	0.2
benzo(g,h,i)perylene	25	15-31	0.4	0.2-0.6	BDL	–	BDL	–	0.2
indeno(1,2,3-c,d)pyrene	4.3	2-6	BDL	–	BDL	–	BDL	–	0.1

* *mg/kg dry weight of soil*

BDL *below detection limits*

** *samples from the 6" to 12" depth were not analyzed*

+ *detection limit of the analytical procedures used*

Wood Treating Site (WTS) Site --

The sludge applied at this site had been applied in 1985 in two applications (Section 3) and the plot was tilled bi-weekly to mix and aerate the surface soils. Detectable concentrations of all 16 PAH compounds except acenaphthalene and acenaphthene were in the top layer (0-6") of the soil (Table 5.5). The detectable concentrations of PAH below the 0-6" layer were very low (near detection limits) indicating that little or no migration had occurred below this depth. An O/G determination was not performed on the samples collected from this site because this parameter is not relevant for the type of wastes that were applied (creosote residues).

Niagara Mohawk Power Corporation (NMPC) Site --

The wastes at this site had been removed from where they had been initially placed, deposited at this site in the early 1960's, and covered with topsoil (Section 3). The wastes were not well mixed into the soil when they were placed in the trench.

TABLE 5.4 PAH CONCENTRATIONS* AT THE CONOCO SITE
(Samples from the 0-6" Depth)

Compound	5% Plot	10% Plot	15% Plot	Detection Limit+
naphthalene	11	8.0	6.9	1.0
acenaphthalene	BDL	BDL	BDL	2.0
acenaphthene	BDL	16	16	1.0
fluorene	0.7	BDL	1.0	0.2
phenanthrene	3.6	6.3	4.5	0.1
anthracene	BDL	0.3	0.5	0.1
fluoranthene	BDL	BDL	BDL	0.2
pyrene	BDL	19	13	0.1
benzo(a)anthracene	BDL	7.9	7.2	0.1
chrysene	4.8	7.8	5.9	0.1
benzo(b)fluoranthene	3.8	6.0	5.1	0.2
benzo(k)fluoranthene	1.6	BDL	1.3	0.1
benzo(a)pyrene	9.0	17	12	0.1
dibenzo(a,h)anthracene	19	49	37	0.2
benzo(g,h,i)perylene	11	28	25	0.2
indeno(1,2,3-c,d)pyrene	3.6	6.6	4.3	0.1

* *mg/kg dry weight of soil*
BDL *below detection limits*
+ *detection limit of the analytical procedures used*

This is apparent by the distribution noted in Table 5.6. This random pattern of constituents as a function of depth in the soil profile also is shown in the metals concentration data presented in the next section.

METALS

The soils were analyzed for cadmium, chromium, copper, lead, nickel, and zinc as noted in Section 4.

Texaco (Anacortes) Site --

Cadmium was not found in these soil samples at concentrations above the detection limit of 10 mg/kg dry weight. The concentrations of the other five metals in these soils as a function of depth are summarized in Table 5.7. The analyses indicated that these metals are concentrated in the top soil depths. As noted earlier (Section 3), at the location where the oil core samples were taken, the surface of the HWLT plot had increased about 26 inches. Thus the highest concentrations of the metals are with the accumulated treated waste residues at this site.

TABLE 5.5 PAH CONCENTRATIONS* AT THE WTS SITE
(mg/kg dry weight of soil)

Compound	Sample Depth 0-6"	12-24"	24-36"	36-54"	Detection Limit+
naphthalene	3.1	BDL	BDL	BDL	1.0
acenaphthalene	BDL	BDL	BDL	BDL	2.0
acenaphthene	BDL	BDL	BDL	BDL	1.0
fluorene	9.3	BDL	BDL	BDL	0.2
phenanthrene	1.1	0.3	0.1	0.1	0.1
anthracene	1.2	BDL	BDL	BDL	0.1
fluoranthene	20	0.4	BDL	BDL	0.2
pyrene	14	BDL	BDL	BDL	0.1
benzo(a)anthracene	13	BDL	BDL	BDL	0.1
chrysene	20	BDL	BDL	BDL	0.1
benzo(b)fluoranthene	41	BDL	BDL	BDL	0.2
benzo(k)fluoranthene	37	BDL	BDL	BDL	0.1
benzo(a)pyrene	44	BDL	BDL	BDL	0.1
dibenzo(a,h)anthracene	40	BDL	BDL	BDL	0.2
benzo(g,h,i)perylene	24	BDL	BDL	BDL	0.2
indeno(1,2,3-c,d)pyrene	14	BDL	BDL	BDL	0.1

* *from test pit A (Figure 3.5)*
BDL *below detection limits*
+ *detection limit of the analytical procedures used*

TABLE 5.6 PAH CONCENTRATIONS* AT THE NMPC SITE
(mg/kg dry weight of soil)

Compound	Sample Depth 0-6"	12-24"	24-36"	36-54"	Detection Limit+
naphthalene	6.9	BDL	BDL	BDL	1.0
acenaphthalene	BDL	BDL	20	28	2.0
acenaphthene	BDL	BDL	12	BDL	1.0
fluorene	2.9	0.7	24	52	0.2
phenanthrene	1.6	0.2	61	81	0.1
anthracene	BDL	0.2	20	32	0.1
fluoranthene	8.5	2.4	BDL	1.4	0.2
pyrene	6.9	2.2	BDL	160	0.1
benzo(a)anthracene	BDL	1.4	15	27	0.1
chrysene	5.7	1.4	10	19	0.1
benzo(b)fluoranthene	8.4	1.6	3.4	7.6	0.2
benzo(k)fluoranthene	7.5	1.1	2.4	5.5	0.1
benzo(a)pyrene	13	1.7	7.0	15	0.1
dibenzo(a,h)anthracene	13	1.8	BDL	1.1	0.2
benzo(g,h,i)perylene	8.3	1.1	1.4	4.1	0.2
indeno(1,2,3-c,d)pyrene	34	1.2	2.4	5.3	0.1

* *from test pit A (Figure 3.6)*
BDL *below detection limits*
+ *detection limit of the analytical procedures used*

TABLE 5.7 AVERAGE METAL CONCENTRATIONS IN THE TEXACO, ANACORTES SOIL CORE SAMPLES (mg/kg dry weight of soil)*

Depth	Chromium	Copper	Lead	Nickel	Zinc
0-6"	280	110	130	110	235
6-12"	320	160	140	100	250
12-24"	180	60	70	100	150
24-36"	130	20	5	55	55
36-54"	140	30	5	60	60
54-72"	120	35	5	65	68

* *average values of triplicate samples*

The metal concentrations of the deeper soil samples from this study are compared to background soil concentrations in Table 5.8. Based on the three metals that were measured in both studies, the Cr and Ni concentrations in the soils from this study are greater than those in the background soils. The Pb concentrations in deeper soils from this study were comparable to that of background soils.

TABLE 5.8 METAL CONCENTRATIONS (mg/kg) IN SOIL CORES FROM THIS STUDY AND IN BACKGROUND SOILS – TEXACO, ANACORTES SITE

Metal	This Study (Table 5.7 – 24-72" soil samples)	Background Soils (Table 3.5 – 36-72" soil samples)
Chromium	120-140	38-39
Lead	5	ND-10
Nickel	55-65	33-43

When the data from this study are compared to that of previous data from this HWLT site, the comparison (Table 5.9) indicates: (a) the ZOI Cr concentrations are similar, (b) the Pb ZOI concentrations of the samples from this study were greater than those of the previous study and (c) the Ni concentrations of samples from this study were less than those of the previous study.

TABLE 5.9 METAL CONCENTRATIONS (mg/kg) in ZOI (0-12") SAMPLES FROM THIS STUDY AND FROM A PREVIOUS STUDY – TEXACO, ANACORTES SITE

Metal	This Study+ (Table 5.7)	Previous Study++ (Table 3.5)
Chromium	280-320	286
Lead	130-140	72
Nickel	100-110	338

+ *average value of triplicate samples*
++ *average of data from the 1985, 1986, and 1987 studies*

Conoco (Ponca City) Site--

These soil samples did not have cadmium concentrations in excess of the detection limit of 10 mg/kg dry weight. The concentration of the other five metals as a function of depth are presented for the three Conoco plots.

The Conoco site has had similar types of wastes applied as at the Texaco site, although in smaller total quantity. The last waste application to the test sites was in 1978 and the wastes had been subjected to nine years of natural treatment prior to sampling for this research. The total metals analyses for the Conoco site indicated the presence of the same five metals as at the Texaco site, chromium, copper, lead, nickel and zinc; however, the metals were primarily in the top 6-12 inches of the soil, as opposed to the surface 24 inches at the Texaco site. This difference is probably a function of the build-up of the ZOI in Texaco soils.

The 10% plot samples had the highest concentrations of metals, suggesting that this plot had had wastes applied which were higher in metals than the wastes applied to the other plots. This is not what the site information had indicated (Section 3). Figure 5.3 portrays the concentration of chromium, lead, and zinc in these soils as a function of depth after 9 years of closure at this site.

Table 5.11 compares the metal concentrations in the deeper soil cores of this study to those in the background soils. The comparison indicates that, except for Cr in the 15% plots, the metal concentrations in the soils below the top 24 inches of the research site were similar to those in the background soils.

TABLE 5.10 AVERAGE METAL CONCENTRATIONS IN THE CORE SOIL SAMPLES OF THE CONOCO 5%, 10% AND 15% PLOTS – (mg/kg dry weight of soil)[*]

Depth	Chromium	Copper	Lead	Nickel	Zinc
5% Plot					
0-6"	490	250	1350	50	770
6-12"	150	42	46	30	200
12-24"	90	13	<1	40	78
24-36"	28	15	21	35	58
36-54"	27	13	14	36	58
54-72"	29	12	16	37	49
10% Plot					
0-6"	1160	425	2140	45	1050
6-12"	150	45	180	28	115
12-24"	68	13	23	36	65
24-36"	27	13	170	34	57
36-54"	30	12	15	30	50
54-72"	27	10	10	34	50
15% Plot					
0-6"	820	294	1460	35	800
6-12"	150	44	178	28	68
12-24"	66	12	22	27	58
24-36"	65	9	18	31	59
36-54"	63	9	13	29	54
54-72"	63	8	17	34	51

[*] *average of triplicate samples*

TABLE 5.11 METAL CONCENTRATIONS (mg/kg dry weight) IN SOIL CORES FROM THIS STUDY AND IN BACKGROUND SOILS – CONOCO SITE

Metal	This Study[+] (Table 5.10 – 24-72" soil samples)	Background Soils[++] (Table 3.11 – 0-18" soil samples)
Chromium	27-65	18-20
Copper	8-15	12-15
Lead	10-21[*]	20-23
Nickel	27-40	19-23
Zinc	29-58	45-54

[+] *average of triplicate samples*

[++] *from 1976 study*

[*] *concentration of one sample not included in the noted range was 170 mg/kg*

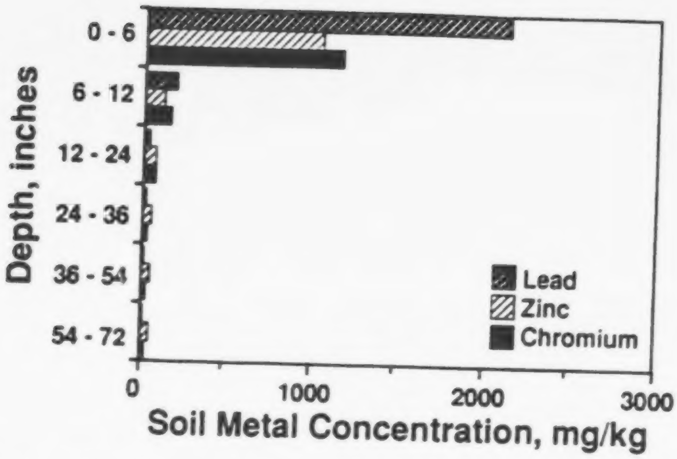

FIGURE 5.3 SOIL METAL CONCENTRATION (mg/kg dry weight) AS A FUNCTION OF DEPTH – CONOCO (10% SITE)

Wood Treating Site (WTS) --

The soils sampled at this site came from a test plot established in 1985 as part of a Land Treatment Demonstration site. The metal concentrations found in the soils cores at this site are summarized in Table 5.12. Cadmium concentrations were not found in these soils above the detection limit of 10 mg/kg dry weight. Figure 5.4 indicates the results for nickel and zinc, the metals in highest concentrations. Pits A, B, and C identify the three separate sampling pits at this site (Figure 3.5).

Unfortunately, no data identifying site background soil metal concentrations were available so it is difficult to interpret the metals data shown in Table 5.12 and Figure 5.4. Based on the method of sludge application, the PAH concentrations in this test plot (Table 5.5), and the metal concentrations found at the other HWLT sites (Tables 5.7 and 5.10), it was expected that the highest metal concentrations would be found in the surface soils. The expected pattern of decreasing metal concentrations as a function of depth noted in the Texaco and Conoco samples was not observed with the WTS samples.

The sludge applied to this test plot did not have high concentrations of metals (Table 3.13). The metal concentrations in the WTS soils (Table 5.12) generally are

TABLE 5.12 AVERAGE METAL CONCENTRATIONS IN THE WTS SOILS
(mg/kg dry weight of soil)*

Depth	Chromium	Copper	Lead	Nickel	Zinc
0-6"	8.6	7.7	5.4	28	40
6-12"	8.4	8.6	5.5	27	37
12-24"	7.6	8.1	5.3	23	45
24-36"	5.7	7.1	5.5	16	50
36-54"	6.2	5.4	1.6	20	75
54-72"	7.5	5.7	2.2	16	25

* *average values of triplicate samples*

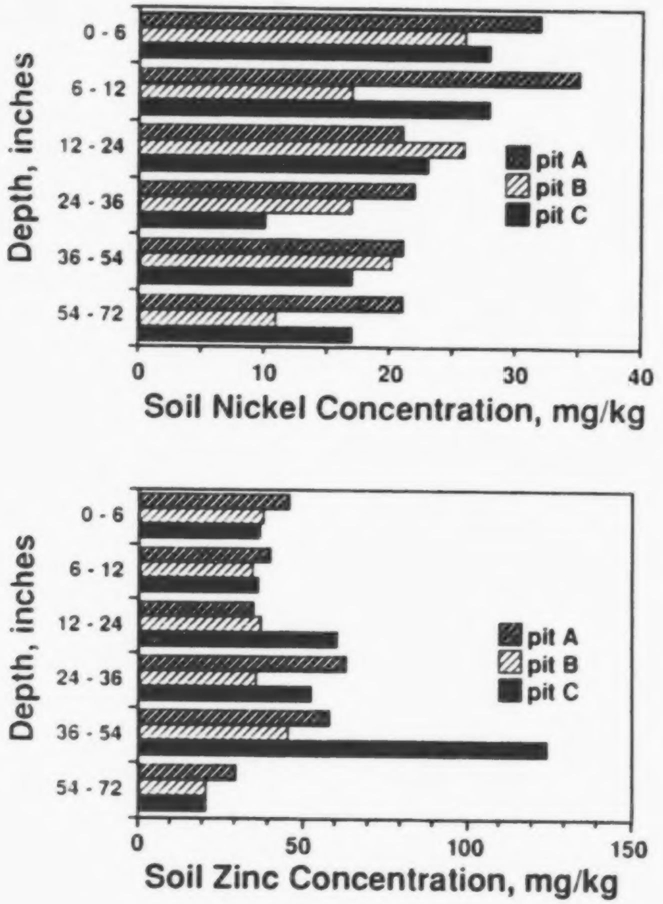

FIGURE 5.4 NICKEL AND ZINC CONCENTRATIONS (mg/kg dry weight) IN THE WTS SOILS AS A FUNCTION OF DEPTH

less than the concentrations in the sludge (Table 3.13). It is speculated that the metal concentrations in the WTS soils, especially in the soils below the tilling depth of about 12 inches, represent background soil concentrations rather than migration of these metals. This speculation is supported by the fact that lead concentrations in subsurface soils from a site near the test plots were in the same range (2.5-10.2 mg/kg) (Table 3.15) as those found in WTS test plot soils (1.6-5.5 mg/kg) (Table 5.12).

Niagara Mohawk Power Corporation (NMPC) Site --

As discussed in Section 3, the chemicals in the site soil samples were the residues from coal tars that had accumulated for an extremely long period of time prior to being disposed of at this site. The wastes were placed in a trench and were not incorporated into the soil at the site. The results of the metals analyses confirm the non-uniform incorporation of the residues. The method of residue placement makes it difficult to determine the extent of metals attenuation at this site.

Cadmium in these soils was not in excess of the detection limit of 10 mg/kg dry soil. The analyses for the other five metals are summarized in Table 5.13.

TABLE 5.13 AVERAGE METAL CONCENTRATIONS IN THE NMPC SOILS (mg/kg dry weight of soil)*

Depth	Chromium	Copper	Lead	Nickel	Zinc
0-6"	7.8	1.7	2.0	5.9	6.3
6-12"	1.0	1.8	1.6	3.1	BDL
12-24"	5.6	1.7	2.0	5.6	6.4
24-36"	9.6	2.8	12	4.5	30
36-54"	3.1	2.6	5.9	4.2	20
54-72"	2.6	3.0	5.4	3.8	18

* *average values of triplicate samples*

SUMMARY

PAH, oil and grease, and metals were found in the site samples. The data indicated that at the Texaco and Conoco sites, these constituents accumulated in the surface soils. There appeared to be little migration to lower depths. The difference in the NMPC data is due to the fact that the applied residues were placed in a trench rather than being incorporated in surface soils.

Of the six metals evaluated, cadmium was not found in concentrations above detection limits at any site.

SECTION 6

SAMPLE VARIABILITY STUDIES

At HWLT sites, the site soil characteristics will have a natural variability that is due to the different wastes that have been applied and the waste application patterns that occurred. Knowledge of such variability is important to decisions with regard to how representative one or more samples may be and site characterizations and monitoring decisions (how many samples to take and what parameters should be monitored). For this study, an evaluation of site variability was needed to determine whether the small number of core samples taken and analyzed were reasonably representative of the site.

Therefore, as noted in Section 3, separate surface soil samples were taken from the Anacortes and the Conoco sites to determine the variability in characteristics that may exist in the surface soils at a HWLT site. The samples and analyses were evaluated to determine whether the core samples, with respect to the samples from the ZOI, were representative of the waste residues at these two sites. In addition, the results from this sample variability study can provide information on the extent to which one or more samples taken from the ZOI of a HWLT are representative of the average characteristics at a site.

Twelve samples were taken from the ZOI at the Anacortes site and at each of the Conoco 5, 10 and 15% plots. The locations of these ZOI samples are noted in Figures 3.2 and 3.4 respectively. The wastes applied to these sites, the length of time they were used, and other information pertinent to the sites are presented in Section 3. Resources did not permit analysis of all of the constituents that could be in the samples. Therefore, the ZOI samples were analyzed for organic matter, dry weight, freon extractables, and three metals (copper, chromium and iron), using the procedures identified in Section 4. These parameters represent compounds that are part of soil and of the wastes that were applied and accumulated in the surface soils. The data from these analyses were compared using standard statistical tests to determine whether there was a difference in chemical characteristics between the sampling locations.

TEXACO

The Texaco Anacortes ZOI samples were obtained from locations that were determined in a random manner (Figure 3.2) using random coordinates generated by a hand-held calculator. The selected spots were marked and the surface vegetation at these sampling locations was scraped away. The upper six inches of soil were collected as the ZOI samples with a hand trowel, placed in separate 250 mL glass jars equipped with Teflon-lined caps, given identification numbers, and shipped to the EWRE-UT Laboratory where they were stored at 4° C until analyzed.

The analyses of the twelve ZOI samples for the noted parameters are shown in Tables 6.1 and 6.2.

TABLE 6.1 SOLIDS AND OIL AND GREASE IN THE ZOI SAMPLES FROM THE TEXACO SITE

Sample	% Dry Weight	% Volatile Solids	mg O/G / kg Dry Weight
1	77	11.5	26,300
2	78	10.3	67,000
3	75	10.4	46,800
4	75	12.7	37,700
5	78	16.4	64,500
6	76	10.9	41,300
7	78	10.2	58,800
8	70	13.8	56,600
9	74	11.6	53,000
10	66	11.3	25,200
11	75	9.6	18,200
12	77	9.7	20,500
Average	75	11.5	43,000
Standard Deviation	2	1.9	17,400

CONOCO

The ZOI samples obtained from the Conoco site were obtained in the following manner. Twelve ZOI samples were selected from each of the three sections in the Conoco land treatment site. Each section was 25 by 20 feet and was marked off in 5-foot (1.5 m) increments (Figure 3.4) to form a sampling grid. Samples were taken at points where the grid lines intersected. Grasses were removed with a shovel. The 0-6" layer was sampled with a hand auger and each sample placed in a sealable plastic bag. The soil was mixed by shaking the bag and was transferred to a 250 mL glass jar sealed with a Teflon-lined cap. The jars were given identification numbers and shipped to the EWRE-UT Laboratory where they were stored at 4°C until analyzed.

The solids and freon extractable (oil and grease) results for the ZOI samples for the plot are indicated in Tables 6.3 to 6.5. Results for the Cu, Cr and Fe concentrations in the ZOI samples of the plots are presented in Tables 6.6 to 6.8.

TABLE 6.2 COPPER, CHROMIUM, AND IRON CONCENTRATIONS(+) IN THE ZOI SAMPLES FROM THE TEXACO SITE

Sample	Copper	Chromium	Iron
1	120	420	20,300
2	95	330	22,200
3	250	490	28,200
4	110	430	20,800
5	570	420	29,700
6	110	400	20,700
7	280	390	18,500
8	140	490	18,300
9	120	370	16,000
10	38	99	12,600
11	130	340	16,900
12	50	200	17,000
Average	170	360	20,000
Standard Deviation	140	110	4,700

+ *mg/kg dry weight*

TABLE 6.3 SOLIDS AND OIL AND GREASE IN THE ZOI SAMPLES FROM THE 5% CONOCO SITE

Sample	% Dry Weight	% Volatile Solids	$\frac{\text{mg O/G}}{\text{kg Dry Weight}}$
1	84	5.4	3,130
2	84	4.7	3,740
3	85	5.5	4,700
4	85	5.9	3,350
5	85	5.2	5,920
6	87	5.3	3,150
7	89	5.3	3,900
8	91	5.8	3,720
9	86	4.8	2,120
10	85	4.5	3,500
11	88	5.0	3,980
12	90	5.2	2,850
Average	86	5.2	3,670
Standard Deviation	2	0.4	915

TABLE 6.4 SOLIDS AND OIL AND GREASE IN THE ZOI SAMPLES FROM THE 10% CONOCO SITE

Sample	% Dry Weight	% Volatile Solids	mg O/G / kg Dry Weight
1	88	7.2	12,900
2	84	8.3	15,000
3	82	6.5	13,000
4	87	7.1	10,100
5	86	7.7	11,600
6	87	7.9	20,400
7	88	8.1	14,800
8	88	7.1	9,200
9	88	7.8	10,400
10	85	7.9	18,300
11	82	8.6	18,300
12	87	7.7	11,600
Average	86	7.7	13,800
Standard Deviation	2	0.6	3,500

TABLE 6.5 SOLIDS AND OIL AND GREASE IN THE ZOI SAMPLES FROM THE 15% CONOCO SITE

Sample	% Dry Weight	% Volatile Solids	mg O/G / kg Dry Weight
1	88	8.2	14,400
2	82	8.2	13,600
3	83	7.6	16,100
4	82	6.3	16,800
5	87	7.8	8,400
6	85	8.1	13,400
7	86	7.4	17,400
8	82	7.3	17,700
9	88	7.6	15,500
10	82	6.9	15,400
11	88	7.2	17,800
12	86	6.5	13,500
Average	85	7.4	14,000
Standard Deviation	3	0.6	2,600

TABLE 6.6 COPPER, CHROMIUM, AND IRON CONCENTRATIONS(+) IN THE ZOI SAMPLES FROM THE 5% CONOCO SITE

Sample	Copper	Chromium	Iron
1	220	540	14,200
2	210	510	14,500
3	260	640	14,900
4	290	730	15,800
5	390	850	16,600
6	370	860	25,400
7	250	620	15,400
8	330	770	16,500
9	170	490	14,600
10	210	560	14,000
11	240	610	15,600
12	350	710	14,000
Average	275	660	16,000
Standard Deviation	70	120	2,970

+ *mg/kg dry weight*

TABLE 6.7 COPPER, CHROMIUM, AND IRON CONCENTRATIONS(+) IN THE ZOI SAMPLES FROM THE 10% CONOCO SITE

Sample	Copper	Chromium	Iron
1	390	950	17,600
2	400	940	17,300
3	330	830	16,800
4	290	800	16,300
5	440	1,000	17,600
6	440	990	17,500
7	410	940	16,900
8	450	1,100	17,600
9	380	850	16,400
10	440	870	17,200
11	420	980	16,100
12	450	1,100	17,400
Average	400	950	17,100
Standard Deviation	50	80	500

+ *mg/kg dry weight*

TABLE 6.8 COPPER, CHROMIUM, AND IRON CONCENTRATIONS(+) IN THE ZOI SAMPLES FROM THE 15% CONOCO SITE

Sample	Copper	Chromium	Iron
1	310	850	16,000
2	320	880	16,400
3	290	800	15,300
4	270	780	17,100
5	350	890	16,000
6	360	980	17,100
7	310	890	15,400
8	250	860	13,800
9	380	950	16,200
10	350	960	15,500
11	280	780	14,300
12	440	820	22,200
Average	330	870	16,300
Standard Deviation	50	65	2,000

+ *mg/kg dry weight*

RESULTS

The Conoco data offer the opportunity to evaluate the differences between plots that had different application rates. Table 6.9 summarizes the data for dry weight and volatile solids (an estimate of organic matter content) in the ZOI samples. No difference in the dry matter content (% dry weight) of the samples from the different plots existed. The average dry matter content ranged from 85 to 86% with a standard deviation of 2 to 3%.

The volatile content of the soil did differ between the 5% plot and the 10% and 15% plots. The % volatile solids averaged 5.2% in the 5% plot and 7.7 and 7.4% in the 10 and 15% plots, respectively. A greater difference between the 10 and 15% plots was expected. Based on the information on waste application that was provided, the volatile content of the 15% plot should have been greater than that of the 10% plot. Either the organic matter applied to the 15% plot in the waste applications weathered more than that in the 10% plot, or the application rates were different than had been indicated.

The Texaco samples (Table 6.1) had a lower dry weight content (75%) than did the Conoco samples (85%). The difference may reflect the different climatic conditions as well as the different water-holding capacities of the two soils.

TABLE 6.9 STATISTICAL VALUES FOR PARAMETERS ANALYZED IN THE ZOI OF THE CONOCO 5, 10 AND 15% PLOTS

Plot and Parameter		Average	Standard Deviation
5% Plot			
	Dry Weight (%)	86	2
	Volatile Solids (%)	5.2	0.4
10% Plot			
	Dry Weight (%)	86	2
	Volatile Solids (%)	7.7	0.6
15% Plot			
	Dry Weight (%)	85	3
	Volatile Solids (%)	7.4	0.6

The Texaco sample also had a much higher average volatile solids content (11.5%) than the Conoco samples (5-7%). This difference may be due to the long use of the Texaco site since the site had been used for 30 years for the land treatment and disposal of refinery wastes and residues as noted in Section 3.

Neither the volatile solids nor the organic matter content of the background soils at the Texaco site or Conoco sites is known (Section 3). The average organic matter of surface soils in the United States varies, but generally is in the range of 2 to 6% in a typical well-drained soil(22). The larger percentages found in the Texaco soils are a result of the organics accumulated from the applied refinery wastes. The increased organic matter in these soils has positive benefits in terms of the transformations and transport of chemicals that have accumulated. These include: (a) increasing the water-holding capacity of the soil, (b) increasing adsorption capability of the soil, thus allowing organics to be retained and be less mobile, and (c) increasing the exchange and sorption capacity of the soil.

The other parameters (Cu, Cr, Fe and freon extractables) are more directly related to the applied wastes. These data were summarized and statistically analyzed to determine the spatial variability of the surface soils and the representativeness of the core samples.

Variation Within Sites

A statistical summary of the results for the Conoco and Texaco ZOI samples are shown in Table 6.10.

TABLE 6.10 SUMMARY OF CONOCO AND TEXACO ZOI ANALYSES[+]

Plot	Statistical Parameter[++]	Copper	Chromium	Iron	Freon Extractables
Conoco					
5% Plot	range	170-390	510-860	13,950-25,380	2,120-5,920
	X±SD	274±71	658±127	15,960±3,100	3,670±956
10% Plot	range	290-460	800-1060	16,100--17,630	9,160-20,400
	X±SD	404±50	948±85	17,050±550	13,800±3,630
15% Plot	range	250-440	780-890	14,300-17,080	8,400-17,800
	X±SD	326±52	870±68	16,270±2,100	14,990±2,650
Texaco					
	range	40-570	100-490	12,600-29,700	18,200-67,000
	X ±SD	157±145	363±114	20,100±4,880	43,000±17,420

[+] *mg/kg dry weight unless noted differently*

[++] *X = mean, SD = standard deviation*

The sampling plan for the Conoco plots followed a 4-row by 3-column pattern. The rows ran in a north-south direction and the columns ran in an east-west direction. This permitted a determination of whether there were variations in the concentrations of the chemicals from row to row or from column to column.

A two way analysis of variance tested the null hypothesis that the variation in the concentrations of each of the chemicals tested in samples taken from different rows or columns was zero. The alternative hypothesis was that significant variation existed from row to row and from column to column. The results of this statistical test were intended to show whether wastes applied to the three plots (5%, 10%, and 15%) were applied uniformly. If the null hypothesis was true, it could be concluded that the wastes had been applied uniformly to the sites.

The analysis of variation was calculated using the Minitab statistical package(23), and the resulting F values are shown in Table 6.11. The normality of the data was tested using NSCORE function and were found to be normally distributed.

The critical value for F was obtained from a statistics table(24) presenting the distribution of F for different degrees of freedom. In this case, the degrees of freedom were representative of the number of rows and columns and the total number of observations. For the Conoco results shown in Table 6.11, there were four rows with P-1 or three degrees of freedom and three columns with two degrees of freedom. For the number of observations ($n = 12$), the degrees of freedom were $[(n - 1) - \Sigma P]$ or six.

Therefore, for the comparison among rows, an F value was obtained for degrees of freedom of 3 and 6 and 95% probability ($F_6^3 = 4.76$) while for the comparison among columns, the F value was obtained for degrees of freedom of 2 and 6 ($F_6^2 = 5.14$) at 95% probability.

TABLE 6.11 ANOVA RESULTS FOR THE CONOCO PLOTS

Sample	Copper	Chromium	Iron	Freon Extractables
Conoco 5%				
Row	0.87	0.76	0.65	0.42
Column	2.62	3.54	2.27	1.09
Conoco 10%				
Row	0.52	0.32	1.34	7.57*
Column	5.81**	2.22	1.72	0.78
Conoco 15%				
Row	0.63	7.89*	0.66	1.71
Column	1.72	4.42	0.38	0.29

* *These values exceed the Critical F of 4.76 ($\alpha<0.05$) showing significant differences exist.*

** *Significant differences ($\alpha<0.05$) existed where F was greater than 5.14.*

The comparison indicated that the null hypothesis was false for only three of the comparisons and that statistically significant differences existed for these three constituents. In the 10% Conoco plot, differences in freon extractable concentrations were observed among the samples taken from the four rows. Differences among columns also were seen for the copper results. The concentration of chromium was different from row to row in the 15 percent plot. There was no consistent pattern to the significant differences that were identified.

In summary, consistent differences in concentrations of the chemicals among the comparisons were not observed. In the four instances where apparent differences were noted, the variation may have resulted from random analytical variability or from spatial variability. A clear distinction between analytical and spatial variability was not determined because replicate analyses of individual samples were not performed. On the basis of the parameters analyzed and samples taken, it appears that the characteristics of the ZOI at the time of the sampling can be considered to be distributed uniformly at the Conoco site.

Variation Among Test Plots

Statistical tests also were performed to determine whether concentrations of the constituents tested were different among the 5, 10 and 15 percent Conoco plots, since the volatile residue data indicated that this appeared to be the case. This determination was made by comparing the means of the constituents in the 5 percent plot to those of the 10 and 15 percent plots using a one-way analysis of variance. A summary of the results of these comparisons is shown in Table 6.12.

The comparison indicated that, for three of the parameters, there was no apparent difference between the 10 and 15% plots. For copper, the 5 and 15% plots had concentrations that were not significantly different. The iron data comparison indicated that there were no iron concentration differences between the three plots. This lack of difference suggests that iron added by the waste applications was only a small fraction of the natural background concentrations and therefore the increases caused by the wastes were not great enough to be distinguished statistically. Iron was included in this evaluation to check the hypothesis that no significant differences would occur. Thus, the use of iron served as a QA/QC check.

TABLE 6.12 SIGNIFICANT DIFFERENCES+ OBSERVED BETWEEN SAMPLE MEANS -- CONOCO 5, 10 AND 15 % PLOTS

Plot	Copper	Chromium	Iron	Freon Extractables
5%	275(a)	658(b)	15,955(a)	3,670(b)
10%	404(b)	948(a)	17,050(a)	13,800(a)
15%	326(a)	869(a)	16,275(a)	15,000(a)

+ *All values are means. Values in the same column with a common letter are not significantly different ($\alpha<0.05$), n=12*

The waste loadings to these plots were indicated to be different, i.e., 5, 10 and 15% total oil in the soil as weight percent. This should have resulted in different concentrations of waste constituents in the plots with the different loadings. However, this evaluation (Table 6.12) did not indicate the expected variation, i.e., higher meta concentrations in the plots with the higher loadings. This comparison reinforces th indication that the actual waste loadings to the plots may not have been as describe (Section 3). This suggestion has little impact on the overall results of the project, except to clarify the conditions of the site from which the core samples were taken for analyses.

CORE SAMPLE REPRESENTATIVENESS

The analyses of the ZOI soil samples can be compared to the analyses of the surface soils (0-6" samples) of the core samples to identify whether the core sample results were representative of the sites. This comparison is presented in Table 6.13.

In most situations, the average value of the core samples was within the range of values of the ZOI samples. However, variation was apparent for metals in some of the plots. To determine whether the differences between the means were significant, a one-way analysis of variance (ANOVA) was performed. This test was used to evaluate the data in Table 6.13 and the F values are shown. The test indicated that only Cr concentrations in the Conoco 10% samples were significantly different than those in the ZOI samples. The Cu concentrations in the 10% plot were statistically the same ($\alpha = 0.05$) in the 0-6" cores and in the ZOI. Concentrations of Cr in the individual 5 and 15% Conoco plots and in the Texaco samples did not vary significantly with location. Similarly, Cu concentrations were unaffected by location and were distributed uniformly in the ZOI.

TABLE 6.13 CONSTITUENTS IN THE ZOI SOILS FROM THE SPATIAL VARIABILITY AND THE CORE SAMPLES

	Concentrations (mg/kg dry weight)				
	Spatial Variability Soils+		Core Samples++		
Constituent	Range	Average	Range (0-6")	Average	F Values*
Texaco					
Copper	40-570	170	250-330	110	0.46
Chromium	100-490	360	630-940	280	1.32
Freon Extractables	18,200-67,000	43,000	+++	61,700	–
Conoco 5%					
Copper	170-390	275	220-270	250	0.30
Chromium	510-860	660	390-550	490	4.65
Freon Extractables	2120-5920	3670	NA	–	–
Conoco 10%					
Copper	290-460	400	400-580	425	0.27
Chromium	800-1060	950	1100-1460	1160	6.26
Freon Extractables	9160-20,400	13,800	+++	5530	–
Conoco 15%					
Copper	250-440	330	250-330	294	0.97
Chromium	780-890	870	630-940	820	0.54
Freon Extractables	8400-17,800	15,000	NA	–	–

+ from Table 6.10

++ from Section 5

+++ only one sample analyzed

NA not analyzed

* values less than the critical F value ($F^{1}_{13} = 4.67$) are not significant ($\alpha = 0.05$)

Assuming that during the operating history of the plots, the relative orientation between the 0-6" layers and the remainder of the cores (to 72") remained constant, then the absence of variability among ZOI samples for the spatial variability samples and the core samples indicates a similar absence of variability for the core samples. Therefore, the characterization data from the core samples are representative of the conditions throughout these HWLT plots at the time of sampling. As a result, the data from the use of the core samples in this study are representative of conditions throughout these sites.

SUMMARY

A statistical analysis of results for parameters measured in ZOI samples collected at two land treatment sites was performed. Within the Texaco and Conoco plots, consistent differences in constituent concentrations at each site were not observed. This may be a consequence of efforts which accomplished uniform application of the wastes at these sites.

The analysis also indicated that the residues that existed at the time of sampling appeared to be uniformly distributed at the site. Thus, if these sites are representative of other HWLT sites and the way they are managed, a large number of soil samples may not be needed to obtain representative data on the characteristics of the soil/residue mixture at closure.

There were instances in which differences for individual constituent concentrations were observed within the Conoco plots. There did not appear, however, to be a consistent trend among the four parameters monitored.

Variation among the three Conoco plots was evaluated. There were no significant differences between the 10 and 15 percent plots for three of the four constituents monitored. These plots were indicated (Section 3) to have had different amounts of waste applied. Either the actual waste application was different than that indicated or the differences between them have lessened since the applications were made.

Based upon a comparison of ZOI soil data and the surface soil samples (0-6") from cores taken at the Conoco and Texaco sites, it appeared that the core samples were representative of the soils at these sites.

SECTION 7

MOBILITY AND WEATHERING STUDIES

The purpose of these laboratory studies was to identify the migration potential of constituents in the site soils. The major objectives were to determine the effects of typical weathering conditions on the constituents present at HWLT sites after the sites have been closed. The effects of simulated weathering cycles on the quality of potential leachate were determined using the TCLP. The primary variables were: (a) soil samples from actual land treatment and contaminated soil sites; (b) soil samples from six depth intervals at each site, starting at the surface and proceeding to six feet below the soil surface; (c) two weathering patterns, Freeze/Thaw and Wetting/Drying cycles, and (d) analyses of TCLP extracts from both weathered and non-weathered samples of soil. The results were used to estimate the migration potential of constituents at sites which contain contaminated soils after closure due to weather patterns.

BACKGROUND

In this study, the term weathering is used to describe the process of soil cycling through periods of climatic conditions such as freezing and thawing, wetting and drying, and the effects such conditions have on the solubility and potential migration of constituents at existing and closed land treatment sites. The atmosphere directly affects a site by providing transport mechanisms for waste constituents and acts indirectly to modify soil-water interactions. Table 7.1 lists relevant atmospheric parameters and their effects.

Weathering is a combination of destruction and synthesis. Both mechanical factors (strains from temperature changes, pressures of freezing water, and erosive action of water, wind, and ice) and chemical factors (hydration, hydrolysis, oxidation, solution, and carbonation) act in the process of weathering. Rocks are broken into smaller rocks and eventually into their individual minerals by weathering. During periods of stress on the soils, the "normal" degradation and immobilization processes of the soil are suspended, or slowed. When the temperature of the soil and its surroundings drop below a certain point, biological activity leading to degradation of organic constituents is significantly decreased. There is little evidence that temperature affects the attenuation of metals(25), but any parameter which restricts the movement of water through the soil profile, including freezing of the available water, also restricts the movement of all constituents in the soil, including metals and organics.

TABLE 7.1 INFLUENCE OF ATMOSPHERIC VARIABLES ON LAND TREATMENT PROCESSES*

Variable	Effect
Temperature	Soil temperature controls microbial population and activity
	Cold temperatures keep soil temperature low, which can limit soil workability and waste degradation, and may increase runoff, lower vapor pressure and decrease volatilization
Precipitation-Evapotranspiration	Controls soil moisture which controls soil aeration, the supply of oxygen for microorganisms, and adequacy of water for microbial activity
	Soil wetness can inhibit field accessibility and enhance the possibility of waste leaching
Winds	Off-site transport of particulates and volatile constituents
	Potential exposure of public by advected particles

* *adapted from reference 3*

When freezing occurs, the ice formed cannot accommodate other atoms or molecules without severe local strain because of the highly organized structure of ice. An ice crystal grows by adding water molecules to its structure, and if a growing crystal comes into contact with other atoms or impurities, it rejects them in favor of water molecules. This process of rejection continues until the accumulated impurities restrict water flow to the crystal.

Meteorological and climatological data are required to assess the public health impacts of chemical migration from land treatment sites to receiving ground and surface waters and via air transmission. These factors also impact the attenuation of chemicals in the soil environment. Should the land treatment soils experience cycles of drying and rewetting, or freezing and thawing, the solubility of the constituents in the leachate can be altered.

Vegetation plays a significant role in soil temperature because of the insulating properties of plant cover. Bare soil becomes very warm during the hottest part of the day, but also rapidly loses its heat during colder periods. A well-vegetated soil during the summer does not become as warm as bare soil, and in the winter, the vegetation acts as an insulator to reduce heat loss from the soil. Frost penetration is more rapid and deeper under bare soils than under a vegetative cover. At closure, a HWLT site may have a cap or vegetative cover over the area, usually to control percolation of additional water. This placement also can moderate the temperature of the soil below the cover.

Several physical characteristics of the soil surface can alter soil temperature. Compaction of the soil surface increases the density and thus the thermal conductivity. Tillage creates a surface mulch which reduces heat flow from the surface to the subsurface. The diurnal temperature variation in a cultivated soil is much greater than in an untilled soil. A loosened soil is colder at night and more susceptible to frost. These factors are relevant to closure and post-closure conditions since tilling procedures could be part of a closure option.

Soil moisture also can have a significant effect on the losses and mobility of constituents at HWLT sites during closure and post-closure. The aerobic biodegradation of organic material in soil is greatest at 50 to 70% of the soil water-holding capacity(2). Inhibition at lower values is due to inadequate water activity, and higher values interfere with soil aeration. One study of the effects of soil moisture content at land treatment sites monitored the rate of evolution of CO_2 at water holding capacities of 30, 60 and 90% for an oil sludge(26). Results indicated the highest rate of carbon dioxide release was at 60%, with the lowest rate at 30%.

Irrigation at land treatment sites increases the heat capacity of the soil, raises the humidity of the air, lowers air temperature over the soil, and increases thermal conductivity, resulting in a reduction of daily soil temperature variations. Sprinkle irrigation, for example, has been used for temperature control, specifically frost protection in winter and cooling in summer, and for reduction of soil erosion by wind. Drainage decreases the heat capacity, thus raising the soil temperature. Elimination of excess water causes a more rapid temperature increase. The addition of humic substances improves soil structure, thus improving soil drainability, resulting indirectly in increased soil temperature. Thus, the increased organic matter that can accumulate at a HWLT site and the routine tilling that has occurred or that may occur under a closure option can directly and indirectly affect the loss and mobility of constituents that remain at closure.

Another factor influencing the magnitude of the effect of moisture on the solubility of both organics and inorganics is the type of soil present and its specific water-holding capacity. The quantity of soil organic matter also influences the adsorption capacity for organic chemicals and metals. Organic matter provides the reducing environment necessary to maintain oxides in their reactive state. This phenomenon is related to the redox potential (Eh) of the soil. Waterlogging of soils can cause a decrease in Eh and increase the availability of many metals. Thus, the variation in seasonal and yearly moisture content at a site contributes to the solubility of the constituents and the type of soil and the closure option used will affect the mobility of organics and metals at closure.

Once the site has undergone closure, vegetation, either planned as a part of the management plan or as natural re-growth over time, will cover the site. This vegetative growth will influence the weathering of the remaining constituents and should be considered when evaluating the impacts of weather on the migration potential of these constituents.

ESTIMATING THE EFFECT OF WEATHERING

Both laboratory evaluations and mathematical models can be used to estimate the effect of weathering conditions on the loss and mobility of soil constituents. Relevant mathematical models, their ability to estimate the effects of weathering, and the results that were obtained in this study are discussed in Section 9. The following paragraphs discuss the laboratory methods and analyses that were used to estimate the effect of weathering.

The objectives of this laboratory weathering study were to: (a) determine the effects of simulated weathering cycles on the quality of leachate (determined by the TCLP) from specific soil samples, (b) evaluate whether these effects were dependent on soil type or waste characteristics and (c) examine the effects of weathering as a function of soil type and depth from the surface. To accomplish these goals, soil samples from several sites were subjected to simulated cycles of weathering, extracted by the TCLP, and analyzed. The first objective was met by comparing the results from the analyses of both the weathered and non-weathered samples for metals and organics. Figure 7.1 depicts the procedures used to meet this objective. The actual steps and sample sizes involved in the weathering procedures are noted in Figure 7.2. The second and third objectives were met by using the results from the TCLP extract analyses in conjunction with the site histories and waste characteristics applied to the soils to look for trends in leachability results.

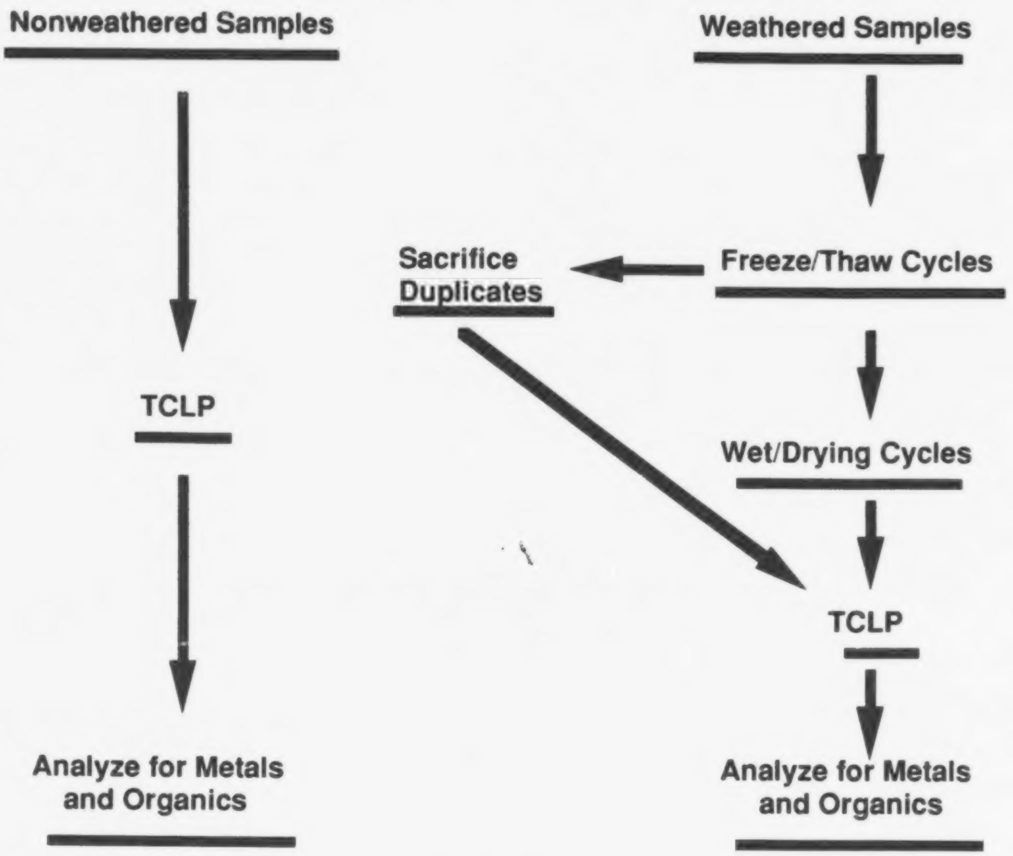
Nonweathered Samples
Weathered Samples
Sacrifice Duplicates
Freeze/Thaw Cycles
TCLP
Wet/Drying Cycles
TCLP
Analyze for Metals and Organics
Analyze for Metals and Organics

FIGURE 7.1 SUMMARY OF TEST PROCEDURES AND SEQUENCE USED IN THE LABORATORY WEATHERING STUDIES

In this evaluation, the following were used: (a) soil from the noted sites, (b) soil samples from six depth intervals, (c) Freeze/Thaw and Wetting/Drying cycles, and (d) analyses of TCLP extracts from both weathered and non-weathered soil samples.

WEATHERING PROTOCOL

The methods used for the simulated weathering cycles were adapted from ASTM methods for tests of soil-cement mixtures. These procedures were used with the soil samples in their as-received state, without the addition of cement. The basic procedure for both of these tests is outlined in Table 7.2.

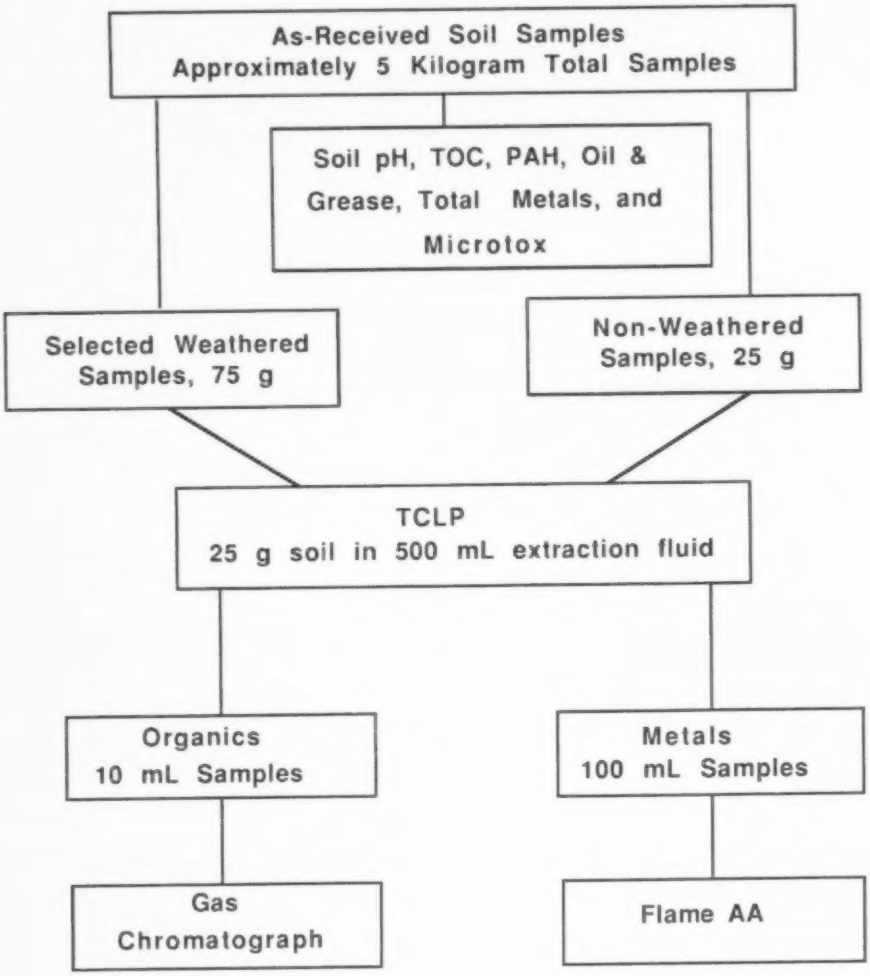
As-Received Soil Samples
Approximately 5 Kilogram Total Samples
Soil pH, TOC, PAH, Oil & Grease, Total Metals, and Microtox
Selected Weathered Samples, 75 g
Non-Weathered Samples, 25 g
TCLP
25 g soil in 500 mL extraction fluid
Organics
10 mL Samples
Metals
100 mL Samples
Gas Chromatograph
Flame AA

FIGURE 7.2 OUTLINE OF STEPS AND SAMPLE SIZES USED IN THE LABORATORY WEATHERING STUDIES

Freeze/Thaw Cycles

ANSI/ASTM D 569[27], "Standard Methods for Freezing-and-Thawing Tests of Compacted Soil-Cement Mixtures" provided the guidelines for the procedure used to subject the soil samples to the simulated climatic variations of freezing and thawing. Modifications in the ASTM procedure were necessary due to the different structure of the samples, i.e., loose soil. However, all of the times and temperatures indicated in procedure were maintained.

The important modification was to contain the soil, and yet allow free exchange of water during the tests. After evaluation, the use of a double-layer of nylon hose was considered suitable. The loss of soil from such a containment was tested and found to be acceptable. The testing consisted of submerging the contained soil in water for 24 hours, drying the contained material, and measuring the weight loss that may have occurred. The average weight loss of four samples was 0.8%.

Prior to use, the samples were sieved, using a No. 9 sieve, to remove large non-soil materials (twigs, stones, roots). Approximately 75 grams of this sieved soil from each of the six depths at the sites were placed into a separate double-layer of nylon, closed and tagged with a label. Table 7.3 indicates the number and location of the soil samples used in the weathering cycles. Duplicate samples of the uppermost and lowest layers (0-to-6 and 54-to-72 inch layers) were included so that one sample from these layers could be sacrificed after the completion of all of the Freeze/Thaw cycles and the other sample could be used in the Wet/Dry cycles (Figure 7.1). Eleven duplicate samples were taken from the Texaco B 12-to-24 inch level to allow for the sacrifice of one sample after each cycle of the Freeze/Thaw test to observe any possible leachate changes, on a cycle-by-cycle basis.

The following provides greater detail about the procedures summarized in Table 7.2. The soil contained in the double layer of nylon was placed on trays lined with four layers of felt, completely submerged in distilled water for 10 minutes and drained of all free water. The samples were then placed into a 100% relative humidity, 73° F constant temperature room. The trays remained in this room for seven days. This step allowed for the complete saturation of all samples to insure that they had the same moisture content.

TABLE 7.2 SUMMARY OF WEATHERING PROCEDURE USED

I. Saturate samples

A. Submerge all samples in water for ten minutes
B. Drain off free water
C. Place samples in a 100% relative humidity, 73°F, constant temperature room for seven days

II. Begin Freeze/Thaw Cycles

A. Place samples in a -10°F, constant temperature room for 24 hours
B. Remove samples from cold room, sprinkle samples with water
C. Place samples (uncovered) in 100% relative humidity, 73° F, constant temperature room for 23 hours
D. Repeat steps A through C a total of eleven times

III. Remove the pre-labelled duplicate samples and place them in storage

IV. Re-saturate samples

A. Submerge remaining samples in water for thirty minutes
B. Drain off free water

V. Begin Wetting/Drying cycles

A. Place samples (uncovered) in a 160° F, 0% relative humidity oven for 42 hours
B. Remove samples from the drying oven and re-saturate for approximately thirty minutes
C. Repeat A and B a total of eleven times

TABLE 7.3 SOIL SAMPLES USED FOR THE WEATHERING CYCLES

Site Identification	Total Number of Test Samples
WTS Plot 1A	8
Conoco A 5%,	8
Conoco A 10%,	8
Conoco A 15%,	8
Texaco A	8
Texaco B	11
NMPC B	8
NMPC C	8

The contained soil was then removed from the 100% humidity, constant temperature room and placed into a -10° F room for 24 hours. At the end of this period, the samples were removed from the cold room, sprinkled with water and placed into a 73° F room for approximately 23 hours. This two-day period of freezing and thawing constituted one cycle of the test. This cycle was repeated for a total of 11 cycles. Twice this cycle was interrupted due to maintenance needs on the 100% relative humidity room and the samples were left in the cold room for 48 hours instead of the specified 24 hours. This contingency of leaving the samples in the freezing phase is outlined in Method D 569(33) as having the least impact on the samples.

The duplicate samples (from the top and bottom layers of each site) were removed from the felt lined trays, re-weighed, and stored at 4°C. These samples, along with the samples from the Anacortes B 12-to-24 inch layer, were then subjected to the TCLP and subsequent metals and organics analysis as previously described. In order to use the same mass of sample as had been used in the original, non-weathered samples used with the TCLP (25 grams at as-received soil moisture content), the weathered samples were increased in mass by a factor of approximately 1.15 times the original 25 grams to compensate for the increased moisture content, as determined from before and after weight measurements.

Wet/Dry Cycles

This procedure is the modified ANSI/ASTM D 559, "Standard Methods of Wetting-and Drying Tests of Compacted Soil-Cement Mixtures"(27). Steps IV and V of Table 7.2 were as follows. The remaining samples were submerged in water for approximately 30 minutes at room temperature, the free water was drained, and the samples were placed in a 160° F, zero percent humidity room for 42 hours. This represented one cycle. The cycles were repeated for a total of 11 times. The samples were then stored in the 4° C room prior to extraction and analysis.

Quality Assurance/Quality Control--

An example set of non-weathered soil samples, showing blanks and spikes used during the procedure, is presented in Table 7.4. The weathered samples were tested in an identical manner. These samples allowed for the determination of contamination, reproducibility, and variation in results.

The TCLP was performed in sets of four, with one blank (TCLP Extract Fluid only, no soil included) included intermittently. This provided a total of 24 blanks for a total of 164 TCLP runs, including both weathered and non-weathered samples. This addition of blanks was to insure data integrity and to check for possible contamination, or carry-over, of results from sample to sample. Additionally, a minimum of one randomly selected duplicate for each set of six depths was tested to verify accuracy and precision of results. These duplicates were treated exactly the same as the original samples and subjected to the same metals and organics analyses as all other samples.

TABLE 7.4 ANALYSES USED WITH SPECIFIC SAMPLES

Sample Location and Depth (in.)	TCLP	Metal	Spiked for Metals	Organics	Spiked Organics
WTS B					
0 - 6"	X	X		X	
6 - 12"	X	X	X	X	
12 - 24"	X	X		X	
24 - 36"	X	X		X	
24 - 36"	X	X		X	
36 - 54"	X	X		X	X
54 - 72"	X	X		X	
BLANK	X	X		X	

One site and depth, Texaco B 12-to-24 inches, was initially sampled in ten duplicate runs of the TCLP, and the leachate was analyzed for metals. This was to test whether the results from one sample from a storage container were the same as those of other samples from the same container and to check for reproducibility of the TCLP results. By sampling one depth repeatedly, an understanding of the impact of sampling variability was obtained. Table 7.5 indicates the results of this evaluation. Excellent reproducibility was obtained for the one situation (Zn) where the metal concentrations were over the detection limits.

In addition to the blank samples from the TCLP, spiked samples of extracts, approximately one in every six samples from a location, were used to check for recovery efficiencies in the metals digestion procedure. Four of the 5 metals analyzed were below the detection limit in all cases. This spiking was accomplished by adding a specific volume of a solution having a known concentration of all six metals to the 100 mL of extract used in the digestion procedure and completing the analytical procedure.

TABLE 7.5 METAL CONCENTRATIONS (mg/L) IN TCLP EXTRACTS OF SOIL SAMPLES+

	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
	<0.1	0.1	<0.1	<0.1	<0.1	1.3
	<0.1	0.1	<0.1	<0.1	<0.1	1.2
	<0.1	0.1	<0.1	<0.1	<0.1	1.5
	<0.1	0.1	<0.1	<0.1	<0.1	1.2
	<0.1	0.1	<0.1	<0.1	<0.1	1.1
	<0.1	0.1	<0.1	<0.1	<0.1	1.3
	<0.1	0.1	<0.1	<0.1	<0.1	1.3
	<0.1	0.1	<0.1	<0.1	<0.1	1.2
	<0.1	0.1	<0.1	<0.1	<0.1	1.2
	<0.1	0.1	<0.1	<0.1	<0.1	1.2
Mean	<0.1	0.10	<0.1	<0.1	<0.1	1.25
S. D.	0	0	0	0	0	0.09

+ soil samples were from the Texaco B test pit, sample depth was 12-24", non-weathered samples

Distilled deionized water (DDW) also was digested, about one in every ten digestions, to determine whether there were any "memory effects", i.e., carry-over of metals from previous digestions, present in the digestion equipment. No carry-over was found.

In addition to the TCLP blank extracts and the duplicate soil samples which were subjected to organic analysis, approximately one in every six extracts was spiked with the 16 PAH compounds and then analyzed. Additionally, any samples which had shown some type of compound on the gas chromatograph runs were reanalyzed using GC/MS to identify the compounds present.

Analytical Procedures

For metals analysis, a mixture of the TCLP extract with concentrated nitric acid (HNO_3) was refluxed in a covered beaker repeatedly, until the mixture was light in color or until its color stabilized. After the mixture had been concentrated to less than 20 mL, it was refluxed with hydrochloric acid (HCl) to dissolve any precipitate or residue remaining. The final volume was brought to 100 mL with distilled deionized water (DDW). The mixture was placed into pre-labelled acid washed storage bottles and stored at 4°C until analyzed using a Flame Atomic Adsorption spectrophotometer.

The TCLP extracts were prepared for organic analysis using SW 846 Method 3510, "Separatory Funnel Liquid-Liquid Extraction"(11). The procedure consisted of taking 100 mL samples from each extract, placing them into 1000 mL separatory funnels, and adding approximately 60 mL of methylene chloride (CH_2Cl_2) to each funnel. The funnel was sealed and shaken vigorously for about 2 minutes with periodic venting to avoid excessive pressures. The organic layer was separated from the aqueous layer by allowing the funnel to stand for a minimum of 10 minutes. The organic (bottom) layer was then drawn off and filtered through approximately 2 centimeters of sodium sulfate to insure that no water would be present in the sample. The extraction was repeated twice more using fresh CH_2Cl_2. The organic layers were then combined for each sample and placed into a Kuderna-Danish concentrator apparatus in a 60°C water bath to concentrate the sample. The final volume of the samples was brought to 10 mL with fresh CH_2Cl_2. This final volume was placed into storage vials and stored at 4°C until analyzed by gas chromatography.

The samples from the liquid-liquid extraction were analyzed on a Hewlett Packard Model 5890A Gas Chromatograph using a Hewlett-Packard 3392A integrator. Selected TCLP samples were spiked with known amounts of specific organics to evaluate the relative abundance of organics present in the TCLP extracts. These added organics were 2,4,6-trichlorophenol, diphenylamine, 2,4-dinitrotoluene, and ortho-cresol. A minimum of three external standards were analyzed prior to each set of extracts being tested, and the best-fit line determined. An internal standard, naphthalene, was used to quantify the results for the spiked samples. During the GC/MS analyses of the TCLP extracts, all peaks were investigated. Any peaks which appeared were identified by library searches of the mass spectrometer data.

The GC was used to determine the concentration of the organics. One microliter of methylene chloride extracts of various samples were injected into the unit with helium as the carrier. The other operating conditions are noted in Table 4.3 and were identical for both the GC and the GC/MS equipment.

RESULTS

TCLP and total sample data are available for all of the site samples(28). However, to avoid unnecessary repetitiveness, the results from one site, the Conoco site, are presented in detail. Also presented are illustrative results from the other sites. The results are summarized in the following sections: (a) organics and metals in the TCLP extracts from the soil samples, and (b) the effects of weathering on the concentration of organics and metals in the TCLP extracts of the weathered samples.

Organics

The GC analyses for the organic constituents of the TCLP extracts, for both the weathered and non-weathered samples, yielded no detectable peaks at any point of the chromatograph analyses, except in the eight samples which subsequently were found to be slightly contaminated as described below. An internal standard, naphthalene, was used in all samples and standards to standardize the resulting peak heights. Four reference chemicals, described in an earlier paragraph, were used in all standards and in approximately every fifth sample as reference peaks for identifying the compounds present in the sample and for estimating the relative concentration of the compound. Minimum Detection Limits (MDL) for these chemicals were determined according to the EPA Quality Control specification(11):

$$MDL = KS_B / m \qquad (7.1)$$

where K = 3 (multiplying factor selected by the EPA)
S_B = standard deviation of the average noise level
m = slope of the calibration line

The limits for the reference chemicals were: 1.86 mg/L for 2,4,6-trichlorophenol, 2.13 mg/L for diphenylamine, 1.94 mg/L for 2,4-dinitrotoluene, and 3.21 mg/L for ortho-cresol. These levels were used to determine the minimum concentration of any organics appearing in the chromatogram.

An example GC chart strip output is given in Figure 7.3. This extract was from the Conoco site, sample A, 15% plot, 6 - 12" depth. The initial large peak at 1.71 to 2.44 minutes was the solvent carrier, methylene chloride, and the peak at 8.14 minutes was the internal standard, naphthalene. The internal standard was at a concentration of 10 mg/L in the sample. The absence of any major peaks other than those due to the solvent and internal standard indicated that the existence of any other organic compound in that extract was slight.

During the GC analysis of the approximately 220 extracts analyzed, 8 samples had some measurable peaks on the chart strip that could be quantified. These samples were analyzed on a mass spectrometer (GC/MS) and the peaks identified by a library search of available chemicals. The results of these scans indicated that 6 of the samples contained phthalates, a common laboratory contaminant, probably from plastic containers used during the methylene chloride extraction procedure. The two remaining samples had peaks which were identified as long-chain hydrocarbon compounds. To verify these results, the soil samples that had

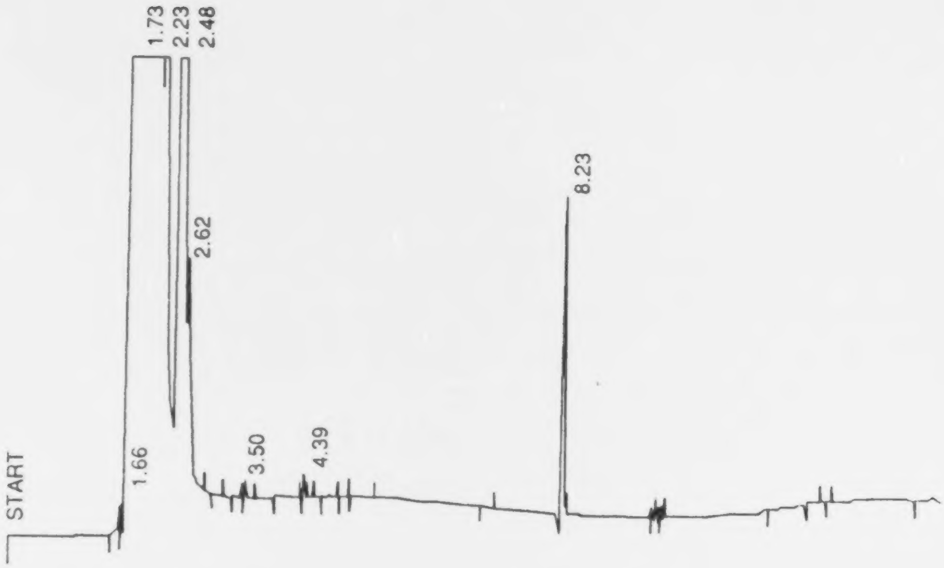

FIGURE 7.3 EXAMPLE GAS CHROMATOGRAPH STRIP CHART OUTPUT OF TCLP EXTRACT, CONOCO SITE, 15% PLOT, 6-12" DEPTH

resulted in these extracts were then re-subjected to the TCLP, extracted and analyzed on the GC/MS. These new extracts had no detectable peaks for either sample. These results suggested that the original TCLP extracts had been contaminated in some manner.

Metals

The following describes the data that resulted from the TCLP extraction of the as-received, non-weathered soil samples. The Conoco (Oklahoma) and the Texaco (Washington state) sites had similar results for the TCLP results. Results for the Conoco site (10 % plot) are presented in Table 7.6.

Figure 7.4 illustrates the decrease in the TCLP extract concentration of chromium, lead and zinc at the Conoco site as a function of depth. The attenuation of these three metals is demonstrated by both the total metals results presented in Section 5 and the TCLP extract analyses (Figure 7.4).

TABLE 7.6 AVERAGE METAL CONCENTRATIONS+ IN THE TCLP EXTRACTS FROM THE CONOCO, 10% PLOT SITE - NON-WEATHERED SAMPLES

Depth	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
0-6"	<0.1	0.2	0.1	0.3	<0.1	2.1
6-12"	<0.1	0.2	<0.1	<0.1	<0.1	0.6
12-24"	<0.1	0.2	0.1	<0.1	<0.1	<0.1
24-36"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
36-54"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
54-72"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

+ *mg/L in extract; detection limit was 0.1 mg/L*

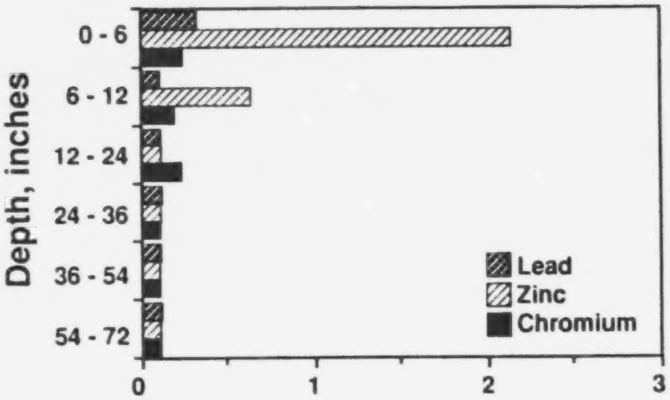

FIGURE 7.4 TCLP EXTRACT METAL CONCENTRATION (mg/L) AS A FUNCTION OF DEPTH: CONOCO 10% SITE

In general, the TCLP extract concentrations at the Texaco, Conoco, and WTS sites as a function of depth were as indicated in Table 7.6 and Figure 7.4. The pattern is one of low concentrations, generally below 1.0 mg/L, in the extract from the surface soils and below detection limits in extracts from the deeper soils.

The one exception was zinc, which in some extracts was above a concentration of 1.0 mg/L. In addition, at the WTS, zinc TCLP extract concentrations did vary with depth (Figure 7.5). For the NMPC site, zinc was consistently above detection limits in all TCLP extracts (Table 7.7).

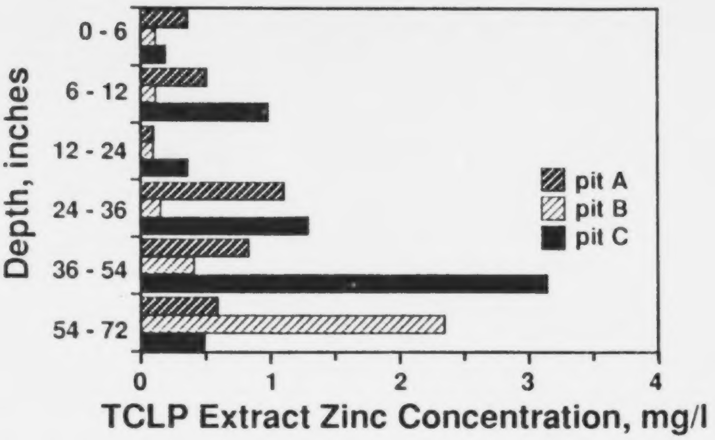

FIGURE 7.5 SOIL ZINC CONCENTRATION (mg/L) AS A FUNCTION OF DEPTH: WTS TEST PITS

TABLE 7.7 AVERAGE METAL CONCENTRATIONS+ IN THE TCLP EXTRACTS FROM THE NMPC SITE - NON-WEATHERED SAMPLES

Depth	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
0-6"	<0.1	<0.1	<0.1	<0.1	<0.1	0.18
6-12"	<0.1	<0.1	<0.1	<0.1	<0.1	0.27
12-24"	<0.1	<0.1	<0.1	<0.1	<0.1	0.27
24-36"	<0.1	<0.1	<0.1	<0.1	<0.1	0.28
36-54"	<0.1	<0.1	<0.1	<0.1	<0.1	0.28
54-72"	<0.1	0.2	<0.1	<0.1	<0.1	0.34

+ *mg/L in extract; detection limit was 0.1 mg/L*

Weathering Cycles

The TCLP extracts of the weathered soil samples had many metal concentration values which were below the detection limit of a specific metal. Therefore, an evaluation of whether a statistically significant difference existed between the weathered and non-weathered samples was not possible. However, there was little change in metals concentration observed in the extracts between the weathered and non-weathered samples. Table 7.8 presents the TCLP extract metal concentrations from the weathered samples from the Conoco 10% plots.

TABLE 7.8 AVERAGE METAL CONCENTRATIONS+ IN THE TCLP EXTRACTS FROM THE CONOCO, 10% PLOT SITE-WEATHERED SAMPLES

Depth	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
0-6"	<0.1	<0.1	0.2	0.5	<0.1	2.1
6-12"	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
12-24"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
24-36"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
36-54"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
54-72"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

+ *mg/L in extract; detection limit was 0.1 mg/L*

Table 7.9 presents the TCLP extract metal concentrations for the samples which were removed from the weathering cycles after completion of the first set of procedures, the freeze/thaw cycles. By testing these duplicate samples and comparing the results with the samples after both the freeze/thaw and wetting/drying cycles were completed, the effects of the individual procedures (freeze/thaw and wetting/drying) were observed. Table 7.10 compares the TCLP extract metals analyses for these duplicate samples. There is no obvious trend in the results of the two procedures. In nine cases, the metals concentration went down between the two procedures and in six cases the concentration went up, leaving no distinctive pattern. Thus, any effects of additional weathering appear to be independent of the type of cycle to which the samples were subjected.

As noted earlier, the TCLP data that resulted from these weathering experiments for all samples were similar. As a result, to avoid unnecessary repetitiveness, only the data from the Conoco site were presented in this section. Therefore, the data that has been presented can be considered representative of that for all of the samples analyzed (Table 7.3).

The results suggest that the effect of further weathering (cycles of precipitation and temperature) on the solubility and mobility of constituents at HWLT sites after closure will be minimal. The petroleum refinery HWLT sites from which the samples were obtained had been in operation or closed for a minimum of ten years.

DISCUSSION

The information in this section on Mobility and Weathering and that in Section 5, Soil/Residue Characteristics, provides an improved understanding of a main objective of this project, i.e., the migration potential of constituents in the residues accumulated at HWLT or similar sites at closure and during post-closure.

Migration Potential

Organics --

PAH were present in the greatest concentrations in the top layers of the soil from the two oil refinery land treatment sites and the wood preserving site. The concentrations of PAH at the coal tar contaminated soil site were in a random pattern due to the placement of the wastes. The only detectable levels of organics found in the TCLP extracts from the sites, either in the as-received soils, or in the samples after they had been subjected to simulated weathering cycles, appeared to result from laboratory chemicals rather than chemicals applied to the soils.

TABLE 7.9 METAL CONCENTRATIONS IN TCLP EXTRACTS (mg/L) -- WEATHERED SAMPLES+

Site++	Depth	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Texaco A	0 - 6"	<0.1	0.2	<0.1	0.2	<0.1	0.48
	54-72"	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
WTS A	0 - 6"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	54-72"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NMPC B	0 - 6"	<0.1	<0.1	<0.1	<0.1	<0.1	0.23
	54-72"	<0.1	0.2	<0.1	<0.1	<0.1	0.89
NMPC C	0 - 6"	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	54-72"	<0.1	0.4	<0.1	<0.1	<0.1	0.21
Conoco A	0 - 6"	<0.1	<0.1	<0.1	0.6	<0.1	1.7
5%	54-72"	<0.1	0.9	<0.1	<0.1	<0.1	0.35
Conoco A	0 - 6"	<0.1	<0.1	<0.1	<0.1	<0.1	2.6
10%	54-72"	<0.1	<0.1	<0.1	0.1	<0.1	0.4
Conoco A	0 - 6"	<0.1	<0.1	<0.1	<0.1	<0.1	2.0
15%	54-72"	<0.1	<0.1	<0.1	0.4	<0.1	<0.1

+ *samples sacrificed after completion of all freeze/thaw cycles; detection limit was 0.1 mg/L*

++ *Descriptions of sample locations are in Section 3.*

The organic analyses data, for both the soil and the TCLP results, indicate that the PAH compounds in these soils have not migrated significantly below the ZOI or the original surface of the soil and, based on the TCLP data, are not likely to have an impact on the groundwater at these sites.

TABLE 7.10 CONCENTRATION (mg/L) OF METALS IN TCLP EXTRACTS
AFTER FREEZE/THAW CYCLES AND WETTING/DRYING CYCLES

Site	Depth	Chromium	Copper	Lead	Nickel	Zinc
Texaco A	0 - 6"+	0.2	<0.1	0.2	<0.1	0.48
	0 - 6"++	<0.1	<0.1	<0.1	<0.1	0.12
	54 - 72"+	<0.1	0.1	<0.1	<0.1	<0.1
	54 - 72"++	<0.1	<0.1	<0.1	<0.1	<0.1
WTS A	0 - 6"+	<0.1	<0.1	<0.1	<0.1	<0.1
	0 - 6"++	0.2	<0.1	<0.1	<0.1	<0.1
	54 - 72"+	<0.1	<0.1	<0.1	<0.1	<0.1
	54 - 72"++	<0.1	<0.1	<0.1	<0.1	0.16
NMPC B	0 - 6"+	<0.1	<0.1	<0.1	<0.1	0.23
	0 - 6"++	<0.1	<0.1	<0.1	<0.1	<0.1
	54 - 72"+	0.2	<0.1	<0.1	<0.1	0.23
	54 - 72"++	<0.1	<0.1	<0.1	0.11	0.33
Conoco A	0 - 6"+	<0.1	<0.1	<0.1	<0.1	2.6
10%	0 - 6"++	<0.1	0.2	0.5	<0.1	2.2
	54 - 72"+	<0.1	<0.1	0.1	<0.1	0.39
	54 - 72"++	<0.1	<0.1	<0.1	<0.1	<0.1

+ *metal concentration after completion of freeze/thaw cycles only*
++ *metal concentration after both freeze/thaw and wet/dry cycles*

Metals --

At the Texaco site, refinery wastes had been applied since 1958, incorporated into the soil and allowed to volatilize, degrade, and become immobilized. The metals data for both the soil residues and the TCLP extracts indicated that the metals have been immobilized primarily in the top 24 inches of the soil At this site, the top approximately 30 inches represents a build-up of residuals and these layers do not include the original ZOI media.

The soil and weather conditions at the Texaco site contribute to the site being a suitable one for land treatment of wastes. The area receives a moderate amount of precipitation (26.6 inches per year), mostly in the form of rainfall, and has moderate temperatures (mean annual temperature is 50.6° F) all year. The characteristics of the soil, a loamy sand, with a near neutral pH, and a high organic matter content (Section 6), indicate good conditions for metal immobilization and organic degradation.

At the Conoco site, the soil conditions and weather patterns were different from those at the Texaco site (Section 3), with warmer temperature, more rainfall, and lower organic matter. The Conoco site had similar types of wastes applied as at the Texaco site, although in smaller total quantity. The last waste application to the tested sites was in 1978 and thus the wastes had been subjected to at least nine years of treatment prior to sampling for this research. The total metals analysis results indicated the presence of the same metals as had been present at the Texaco site, Cr, Cu, Ni, Pb and Zn. Cadmium was not found at concentrations above detection levels. The metals were primarily in the top 6 inches on the soil, as opposed to the top 24 inches at the Texaco site. This difference is probably a function of the build-up of the surface soils at the Texaco site. The 10% plot had the highest concentrations of metals in the surface soils, suggesting that this plot either had wastes applied which were higher in metals than the wastes applied to the other plots or had different amounts applied than originally indicated (Section 3). Figure 7.6 compares the total soil and the TCLP extract concentrations for zinc at this plot.

The Zn concentrations in the core samples of the 10% and 15% plots and in the TCLP extracts from the core samples of the same plots are presented graphically in Figures 7.6 and 7.7, respectively. Both the total Zn concentrations and the TCLP extract concentrations were greatest in the surface soils.

The WTS has soils containing wood-preserving wastes which were from the creosoting of wood. Both the soil analyses and the TCLP results showed a different pattern from that indicated with the Conoco data. The Zn concentrations in the TCLP extracts were plotted in Figure 7.5.

At the NMPC site, the wastes applied were residues from coal tars that had accumulated for an extremely long period of time (Section 3) and had "weathered" to a greater extent than wastes at petroleum industry HWLT sites. The wastes were in a trench and were not incorporated into the soil. Both the soil and the TCLP extract analyses confirmed the random pattern of metals present. The additional simulated weathering of the samples had little effect on the concentration of metals present in the TCLP extract. Metals concentrations were very low, less than 50 mg/kg for the highest metal concentration in the soil and less than 1 mg/L in the TCLP extracts. Because of the waste placement, it is difficult to determine the effects of the weather conditions which exist at this site.

Mass Balance --

To determine the total effect of weathering on constituent mobility and whether there has been any loss of constituents by degradation or to the groundwater at any of the sites, a mass balance on as many constituents as possible must be completed.

The following are necessary to complete such a balance: (a) the total amount of constituents in the applied waste, (b) an estimated amount of the constituent that has volatilized or degraded, and (c) the amount remaining in the soil. However, the applied waste characteristics for these sites were not available and a mass balance was not attempted.

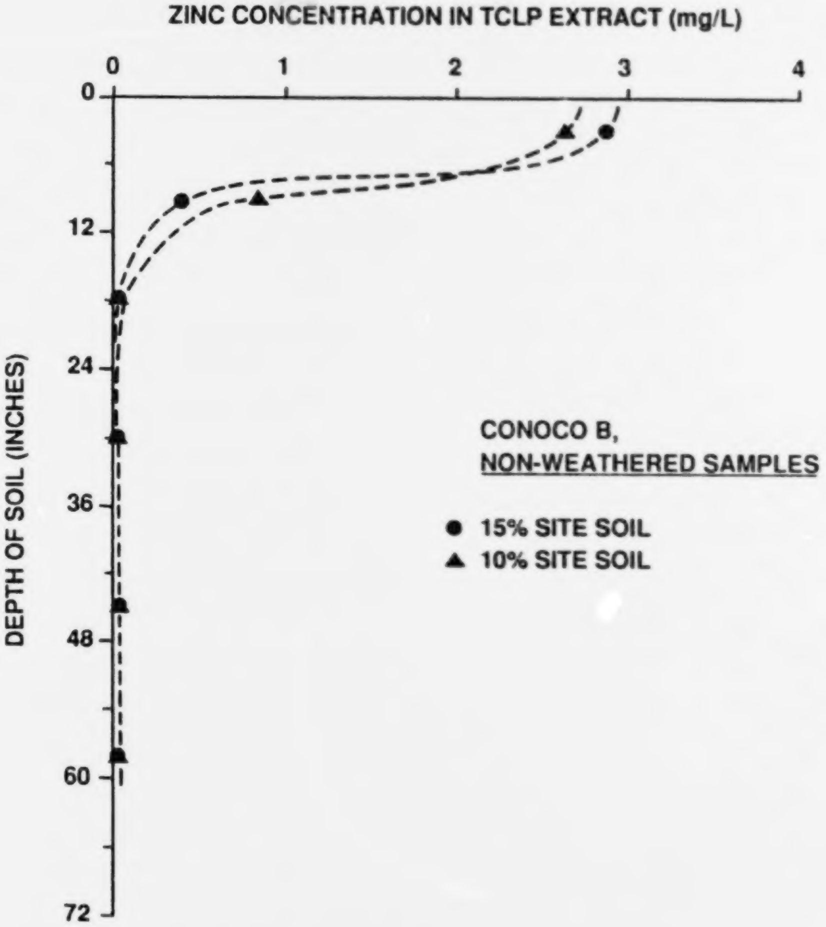

FIGURE 7.6 ZINC CONCENTRATION IN THE CORE SOIL SAMPLES FROM THE CONOCO 10% AND 15% SITES

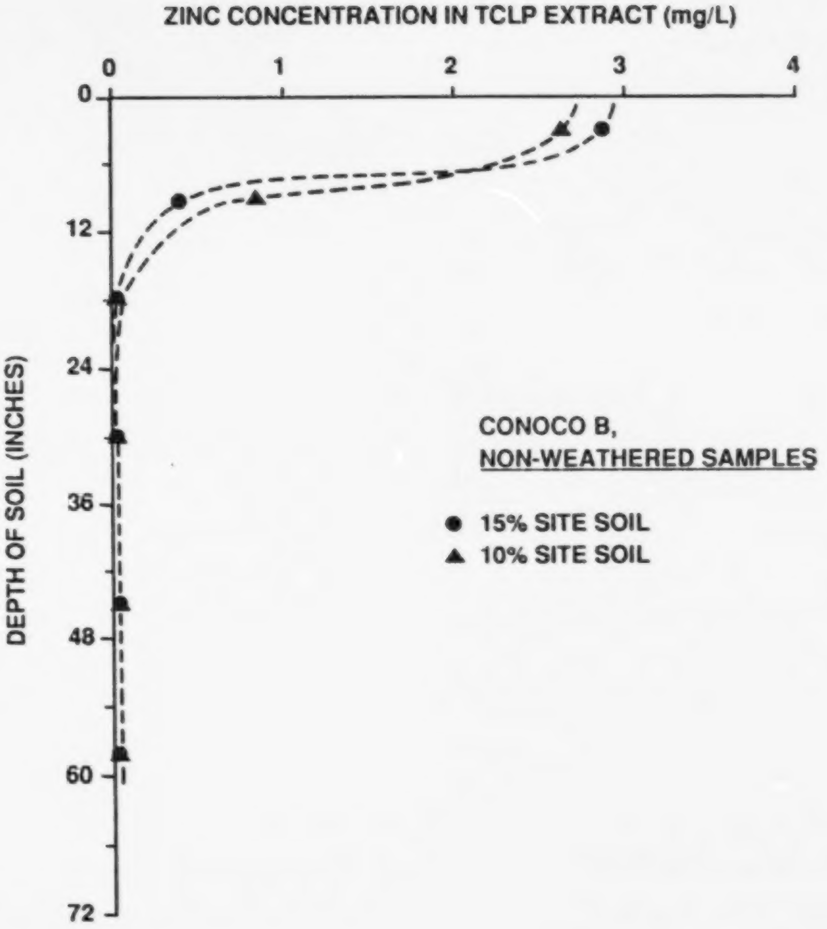

FIGURE 7.7 ZINC CONCENTRATION IN THE TCLP EXTRACTS FROM THE CORE SOIL SAMPLES FROM THE CONOCO 10% AND 15% SITES

Hazardous Characteristics

The land disposal of hazardous wastes is regulated by the Resource Conservation and Recovery Act (RCRA) and its amendments. A waste is a hazardous waste if it meets one of four conditions: (a) exhibits, on analysis, any of the characteristics of a hazardous waste, (b) has been named as a hazardous waste and is listed, (c) is a mixture containing a listed hazardous waste and a non-hazardous solid waste (unless the mixture is specifically excluded or no longer exhibits any of the characteristics of hazardous waste, and (d) is not excluded from regulation as a hazardous waste. The by-products of the treatment of any hazardous waste also are considered hazardous unless specifically excluded or delisted.

Four characteristics classify a waste as hazardous under RCRA: (a) ignitability, (b) corrosivity, (c) reactivity, and (d) extraction procedure (EP) toxicity. The soil and accumulated waste residues that exist at a HWLT site at closure are not expected to exhibit the characteristics of ignitability, corrosivity, or reactivity. Therefore, only the characteristic of EP toxicity is relevant to this material.

The development of the EP Toxicity (EP Tox) test and its predecessors has been outlined(29). The EP Tox test had been developed as a laboratory extraction method for solid wastes that simulated concentrations of inorganic and organic constituents in leachates resulting from codisposal with municipal wastes in landfills with a 95:5 ratio of municipal to industrial wastes, respectively. The EP Tox is a 24-hour batch-type extraction procedure that uses acetic acid to acidify the liquid-solid suspension (20:1 ratio) to a pH of 5.0. The intent of the procedure is to simulate the leaching action of organic acids in municipal waste leachate.

Many laboratory studies were conducted to validate the EP Tox test for different waste types and combinations. However, the validity of the EP Tox test in the determination of hazardous (leachable) constituents has been questioned for many reasons, including the apparent inability of the procedure to extract organics from soil samples, and because the use of acetic acid in the procedure has been shown to interfere with certain aquatic toxicity and phytotoxicity testing protocols.

The importance of the EP Tox test is the following. If the extract from the test contains specified constituents above certain concentrations, the material or waste producing the extract is classified as a hazardous waste. These concentrations represent the uppermost levels of constituents which can be found in the EP Tox test extract before the waste will be classified as a hazardous waste. The test is designed to identify wastes likely to leach hazardous concentrations of particular toxic constituents into the groundwater as a result of improper management.

As noted in Section 4, the TCLP was developed as an improvement of the EP Tox test. Although EPA has not officially replaced the EP Tox test with the TCLP as of the date this report is written, the TCLP is commonly used for regulatory purposes, such as treatment standards for Best Demonstrated Available Technology (BDAT) land disposal restrictions(30,31). Thus, the analyses of TCLP extracts have been used in this project as a measure of relative mobility of chemicals and leachability from soils.

The TCLP data from the project can be analyzed to indicate whether these soil/residues should be considered a hazardous waste. As noted earlier in this Section, the GC analysis for the organic constituents of the TCLP yielded no detectable peaks that were attributable to other than laboratory contamination.

For hazardous waste, a solid waste exhibits the characteristic of toxicity if the liquid extract, obtained using the TCLP procedure, contains concentrations of contaminants that are equal to or greater than the concentrations listed in Table 7.11.

Only cadmium, chromium, and lead are on the list of toxicity characteristic contaminants (Table 7.11). The concentrations identified in Table 7.11 and the highest concentrations found in any of the TCLP extracts are compared in Table 7.12. As noted from the data in the tables in this section, the TCLP extract concentrations in the other samples were considerably less than maximum concentrations noted in Table 7.12. The maximum concentrations found in the TCLP extracts were lower than the concentration of regulatory concern by a factor of 5 to 10.

CONCLUSIONS

The conclusions that can be reached from this laboratory study are the following:

1. Analyses for organics in the TCLP extracts indicated that no PAH compounds were extracted by this procedure from either the weathered or non-weathered soils. Previous data indicated that there were detectable levels of many PAH compounds in the soil samples.

2. There was no apparent difference in the concentration of metals in the TCLP extract of the non-weathered and the weathered samples.

3. The PAH and metal concentrations measured in the TCLP extracts from the soil/residues from these four sites provided no apparent reason to conclude that the soils and accumulated residues would fail to pass a toxicity characteristic determination using the TCLP test and analysis of the TCLP extract.

TABLE 7.11 MAXIMUM CONCENTRATION OF CONTAMINANTS FOR THE HAZARDOUS WASTE CHARACTERISTIC OF TOXICITY

Contaminant	mg/L
Previous List of Contaminants(32)+	
arsenic	5.0
barium	100.0
cadmium	1.0
chromium	5.0
lead	5.0
mercury	0.2
selenium	1.0
silver	5.0
endrin	0.02
lindane	0.4
methoxychlor	10.0
toxaphene	0.5
2,4-D	10.0
2,4,5-TP silvex	1.0
List of Added Constituents(18)	
benzene	0.5
carbon tetrachloride	0.5
chlordane	0.03
chlorobenzene	100.0
chloroform	6.0
o-cresol	200.0*
m-cresol	200.0*
p-cresol	200.0*
1,4-dichlorobenzene	7.5
1,2-dichloroethane	0.5
1,1-dichloroethylene	0.7
2,4-dinitrotoluene	0.13
heptachlor (and its hydroxide)	0.008
hexachlorobenzene	0.13
hexachloro-1,3-butadiene	0.5
methyl ethyl ketone	200.0
nitrobenzene	2.0
pentachlorophenol	100.0
pyridine	5.0
tetrachloroethylene	0.7
trichloroethylene	0.5
2,4,5-trichlorophenol	400.0
2,4,6-trichlorophenol	2.0
vinyl chloride	0.20

+ *prior to March 5, 1990, the concentrations were to be determined by the EP procedure*

* *If, o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol concentration is used. The regulatory level for total cresol is 200.0 mg/L.*

TABLE 7.12 MAXIMUM TCLP EXTRACT CONCENTRATIONS FROM THIS STUDY AND CONCENTRATIONS INDICATING TOXICITY CHARACTERISTICS

Metal	Concentration of Regulatory[**] Concern (mg/L)	Maximum Concentration in TCLP Extract (mg/L)
Cadmium	1.0	<0.1[+]
Chromium	5.0	0.9[++]
Lead	5.0	0.9[*]

[+] *cadmium concentration in all TCLP extracts was below detection limits of 0.1 mg/L*

[++] *Table 7.9*

[*] *Conoco 5% plot weathered sample from 0"-6" depth*

[**] *Table 7.11*

SECTION 8

DEGRADATION STUDIES

In addition to the evaluation of mobility discussed in Section 7, an objective of this project was to identify the extent to which organics remaining at closure of a HWLT or similar site will continue to degrade under closure and post-closure conditions. The closure options (Table 1.1) include: (a) placement of an impermeable cap, (b) no action but continued monitoring, and (c) continued managed in-situ treatment using amendments and enhancements as required. The placement of an impermeable cap will reduce infiltration and leaching but restrict oxygen transfer from the atmosphere. It has been speculated that anoxic or anaerobic conditions under the cover may occur. The other closure options are likely to result in oxidative conditions in the surface soils (Table 1.2).

Because of the expected soil conditions with these closure options, degradation under both aerobic and anaerobic conditions was evaluated. Low rates of degradation were expected and microcosm studies were conducted over an eight-month period. Only samples from the Anacortes ZOI were used. Such samples represent the accumulation of residues over 30 years. The term degradation is used in this section because it was expected that microbial degradation would be the major organic compound loss mechanism. However, the actual loss mechanisms were not investigated.

The procedures for the aerobic and anaerobic microcosm studies were described in Section 4.

RESULTS

Three separate composites of four different Texaco ZOI samples were prepared for two aerobic and one anaerobic degradation microcosm studies since the respective studies were started at different times. The use of initial composites helped assure representative concentrations in each microcosm study. No uncontaminated soil was added to these samples.

The two aerobic studies were: (a) the ZOI soils without amendments or enhancements, and (b) the ZOI soils with additional nitrogen and phosphorus. The nutrients were added to determine whether the addition of nutrients to HWLT soils would have a beneficial effect on the loss of organics in these soils.

Adequate nutrients must be present for optimum microbial activity. A sample of the Anacortes surface soil was tested by a commercial laboratory and found to contain an organic carbon to nitrogen ration of 28:1. To obtain mineralization of the organic carbon, a lower ratio is desired. Thus, nitrogen in the form of ammonium nitrate (NH_4NO_3) was added in an amount to reduce the ratio to 15:1 in the specific microcosms.

The average PAH concentrations throughout the duration of the aerobic, anaerobic and aerobic plus nutrients microcosm studies are presented in Table 8.1, 8.2 and 8.3, respectively. The data in these tables are illustrative of the type of data that results from laboratory microcosm studies with actual soils containing complex mixtures of chemicals. Decreases in chemical concentration should occur with time or there should be no change over time if the organisms cannot metabolize the chemicals or if toxic conditions exist. Toxic conditions were not present in the soils used in the degradation studies.

The data in Tables 8.1 to 8.3 indicate an apparent increase in concentration with time for a number of chemicals. This apparent increase has been seen in numerous other microcosm studies with soils contaminated by complex mixtures of chemicals. The causes for such increases are unknown but are speculated to be: (a) release of organics from soils by microbial surfactants so that the chemicals are more extractable by the solvents used for extraction or (b) other factors that affect the solvent extraction efficiency. Triplicate microcosms were analyzed at each point in time and the data shown in Tables 8.1 to 8.3 are averages of the triplicate analyses. Therefore, sampling and analytical procedure variations were not felt to be a cause of these apparent increases in concentrations.

The differences in the PAH concentrations at the start of each microcosm study (time zero data) (Tables 8.1, 8.2 and 8.3) were due to the fact that different composites of Anacortes ZOI samples were used for each study. The aerobic study was started in August 1988 and the other two studies on two different dates in November 1988. Prior to each study, a composite of the stored Anacortes ZOI soil was prepared, sieved to remove stones and root fragments, and weighed into microcosms used in the respective studies. Thus, although the soils used in these studies were representative of Anacortes ZOI soils, three separate, independent composites were used in each study. Each composite was analyzed separately to determine the initial PAH concentrations for each study.

The freon extractable data for all three studies are presented in Table 8.4. The pH of all the microcosms ranged between 6.0 and 7.1 throughout the studies. There were no discernable trends in the pH data.

TABLE 8.1 AVERAGE PAH CONCENTRATIONS^{+} IN THE COMPOSITE TEXACO ZOI SOIL -- AEROBIC MICROCOSM STUDY

Chemical	Month							Detection Limit
	0	One	Two	Three	Four	Six	Eight	
naphthalene	BDL^{++}	8.0	BDL	BDL	BDL	BDL	BDL	8.0
acenaphthalene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	16.0
acenaphthene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	8.0
fluorene	BDL	2.1	BDL	BDL	BDL	BDL	BDL	1.6
phenanthrene	6	4	4	3	4	3	4	0.8
anthracene	1	BDL	BDL	BDL	BDL	BDL	BDL	0.8
fluoranthene	13	8	8	10	9	**	5	1.6
pyrene	17	11	9	7	7	4	6	0.8
benzo(a)anthracene	9	8	5	4	6	5	3	0.8
chrysene	21	11	14	13	13	8	9	0.8
benzo(b)fluoranthene	13	12	14	54	7	13	9	1.6
benzo(k)fluoranthene	18	17	21	21	22	19	18	0.8
benzo(a)pyrene	8	7	6	9	10	7	6	0.8
dibenzo(a,h)anthracene	17	*	*	*	*	*	*	1.6
benzo(g,h,i)perylene	20	16	15	10	*	*	*	1.6
indeno(1,2,3-c,d)pyrene	16	14	11	14	3	2	1	0.8

$^{+}$ *mg/kg dry weight, average of triplicate analyses; ** peak not detected*

$^{++}$ *BDL = below detection limits; * compound not quantified because of overlap of co-eluting peaks*

It was not clear from visual inspection of the data whether significant losses of the compounds occurred. To ascertain whether losses had occurred, the data were evaluated using analysis of variance (ANOVA) and regression analyses[24,33]. Samples had been collected in triplicate, and the ANOVA was applied first to determine whether statistically significant differences existed among the mean concentrations of each compound in the samples analyzed over time. In experiments of this type, degradation or loss of organics such as PAH or freon extractables should be reflected by decreases in concentration at each successive sampling, and these changes, if significant would be detected by the ANOVA. In this study, only statistically significant decreases in concentration over time are relevant and indicated that degradation or loss occurred in the microcosms.

TABLE 8.2 AVERAGE PAH CONCENTRATIONS^{+} IN THE COMPOSITE TEXACO ZOI SOIL -- ANAEROBIC MICROCOSM STUDY

Chemical	Month							Det. Limit
	0	One	Two	Three	Four	Five	Eight	
naphthalene	BDL^{++}	BDL	BDL	BDL	23	BDL	BDL	8.0
acenaphthalene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	16.0
acenaphthene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	8.0
fluorene	2	2	BDL	BDL	BDL	BDL	BDL	1.6
phenanthrene	5	5	7	8	6	6	4	0.8
anthracene	1	1	1	2	1	BDL	BDL	0.8
fluoranthene	15	6	10	13	11	12	10	1.6
pyrene	8	17	23	22	15	17	9	0.8
benzo(a)anthracene	10	11	17	18	18	22	12	0.8
chrysene	22	20	23	24	22	22	13	0.8
benzo(b)fluoranthene	12	10	11	12	10	11	5	1.6
benzo(k)fluoranthene	15	16	21	26	24	26	15	0.8
benzo(a)pyrene	3	4	7	10	11	6	4	0.8
dibenzo(a,h)anthracene	24	35	29	•	26	44	24	1.6
benzo(g,h,i)perylene	46	45	44	54	51	76	28	1.6
indeno(1,2,3-c,d)pyrene	5	2	13	15	11	10	16	0.8

$^{+}$ *mg/kg dry weight, average of triplicate analyses*
$^{++}$ *BDL = below detection limits*
• *peak not detected*

TABLE 8.3 AVERAGE PAH CONCENTRATIONS^{+} IN THE COMPOSITE ANACORTES ZOI SOIL -- AEROBIC PLUS NUTRIENT MICROCOSM STUDY

Chemical	Month							Det. Limit
	0	One	Two	Three	Four	Five	Eight	
naphthalene	BDL^{++}	BDL	BDL	BDL	23	BDL	BDL	8.0
acenaphthalene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	16.0
acenaphthene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	8.0
fluorene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.6
phenanthrene	5	6	4	4	5	3	5	0.8
anthracene	BDL	BDL	BDL	BDL	1	1	1	0.8
fluoranthene	8	11	9	16	14	5	6	1.6
pyrene	11	13	12	11	12	11	11	0.8
benzo(a)anthracene	16	8	16	13	12	6	6	0.8
chrysene	18	11	23	25	24	30	24	0.8
benzo(b)fluoranthene	7	7	9	12	12	19	15	1.6
benzo(k)fluoranthene	21	26	26	28	22	24	18	0.8
benzo(a)pyrene	8	9	8	10	7	2	2	0.8
dibenzo(a,h)anthracene	38	26	36	29	18	9	13	1.6
benzo(g,h,i)perylene	59	93	87	41	41	48	50	1.6
indeno(1,2,3-c,d)pyrene	7	7	7	7	7	4	1	0.8

$^{+}$ *mg/kg dry weight, average of triplicate analyses*
$^{++}$ *BDL = below detection limits*

TABLE 8.4 FREON EXTRACTABLE DATA⁺ IN THE COMPOSITE TEXACO ZOI SOIL -- AEROBIC AND ANAEROBIC LOSS STUDIES

	Month							
Study	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**8**
Aerobic	48,200	43,800	37,800	42,200	35,600	++	35,700	37,100
Aerobic plus nutrients	58,900	55,200	61,400	35,800	46,300	++	40,000	38,600
Anaerobic	52,400	39,100	49,100	45,300	54,000	45,900	++	45,700

⁺*mg/kg dry weight, average of triplicate analyses; ++ sample not analyzed*

The end result of an ANOVA calculation for a set of means is a value for F, where F is a ratio of the variation among means to the variation within the means. Significant variation among the means was indicated when the value calculated for F was greater than the critical value of F. This approach was discussed and used in Section 6.

The ANOVA evaluation only indicates that there were differences among the means but does not indicate whether the differences were due to an increase or decrease with time or were due to a bounce in the data. Of interest in this research were data that indicated losses of a chemical with time, i.e., decreases.

The Q test(33) was used to determine which means were different. This evaluation was performed by calculating the value by which two means would have to differ in order to be significantly different at the 95% level ($\alpha = 0.05$). This value was calculated using a computer spread sheet on Lotus 1-2-3, in which the pooled standard deviation and number of means to be compared were entered. A value for Q was then entered which was obtained from a standard statistical table(33) for the number of means being compared and for the degrees of freedom. The final output of the spread sheet was the minimum difference D which then was used to compare the means. The means were compared by calculating the differences between the respective means, i.e., first and second, second and third, first and third, etc. The calculated differences were then compared to the minimum difference D noted above.

Table 8.5 indicates the results of the ANOVA analyses for the PAH compounds that had concentrations consistently above detection levels. The statistical analyses indicated that significant differences did exist among the mean concentrations of many compounds. The compounds noted in Table 8.5 that exhibited significant differences in mean concentrations were analyzed by the Q test. The results are noted in Table 8.6 for the PAH compounds and in Table 8.7 for the freon extractable data. Also noted in these tables is an indication of the pattern of difference that was indicated, increase, decrease, or no apparent change.

There were very few (five) chemicals for which there was a statistically significant decrease when the means were analyzed by the Q test. For several of these chemicals, the decrease appeared to occur in the last months of the microcosm studies. There was no consistent pattern to the apparent decrease and the small number of significant differences indicated that little, if any, PAH loss occurred in any of the microcosm studies.

TABLE 8.5 ANALYSIS OF VARIANCE SUMMARY OF DEGRADATION DATA

Compounds	Aerobic Study Calculated F	Aerobic With Nutrients Calculated F	Anaerobic Conditions Calculated F
Phenanthrene	1.41	1.15	5.94*
Fluoranthene	1.82	6.43*	0.91
Pyrene	14.38*	1.86	4.72*
Benzo(a)anthracene	6.86*	15.67*	7.42*
Chrysene	2.13	5.05*	7.57*
Benzo(b)fluoranthene	1.42	10.64*	11.09*
Benzo(k)fluoranthene	1.37	6.02*	14.75*
Benzo(a)pyrene	2.46	4.92*	5.97*
Dibenzo(a,h)anthracene	–	3.24	1.86
Benzo(g,h,i)perylene	–	2.88	1.46
Indeno(1,2,3-c,d)pyrene	3.25	8.78*	10.68*
Freon Extractables	0.61	4.65*	4.13*

* *Comparisons in which the one way analysis of variance showed significant variation among the compared means, i.e., calculated F value was greater than the critical F value*

SUMMARY

The degradation studies indicated that there was no statistically significant degradation of PAH and freon extractables in the ZOI soils from the Texaco site over an eight-month period. It was in these soils that the residues from the applied wastes accumulated. The data from this study suggest that there will be very slow degradation of the accumulated organics at closed HWLT sites.

TABLE 8.6 Q TEST EVALUATION* OF MEAN PAH CONCENTRATIONS**

Study and Chemical	Month 0	One	Two	Three	Four	Five	Eight	Difference Pattern***
Aerobic								
Pyrene	17a	11ab	9bc	7bc	7bc	4c	6bc	–
Benzo(a)anthracene	9a	8a	5a	4a	6a	5a	3a	0
Aerobic plus Nutrients								
Fluoranthene	8ab	11ab	9ab	16a	14a	5b	6b	–
Benzo(a)anthracene	16a	8bc	16a	13ab	12ab	6c	6c	–
Chrysene	18b	11b	23ab	25ab	24ab	30a	24ab	0
Benzo(b)fluoranthene	7c	7c	9bc	12bc	12bc	19a	15ab	0
Benzo(k)fluoranthene	21ab	26a	26a	28a	22ab	24ab	18b	0
Benzo(a)pyrene	8a	9a	8a	10a	7a	2b	2b	–
Ideno(1,2,3-cd)pyrene	7a	7a	7a	7a	7a	4b	1b	–
Anaerobic								
Phenanthrene	5ab	5ab	7ab	8a	6ab	6ab	4b	0
Pyrene	18a	17a	23a	22a	15a	17a	9b	0
Benzo(a)anthracene	10c	11bc	17abc	18ab	18ab	22a	12bc	0
Chrysene	22a	20a	23a	24a	22a	22a	13b	0
Benzo(b)fluoranthene	12a	10a	11a	12a	10a	11a	5b	0
Benzo(k)fluoranthene	15c	16bc	21ab	26a	24a	26a	15bc	0
Benzo(a)pyrene	3c	4bc	7ab	10ab	11a	6ab	4bc	0
Ideno(1,2,3-cd)pyrene	5b	2c	13a	15a	11ab	10ab	6bc	0

* *means with a common letter in the same row are not significantly different (α = 0.05)*
** *mg/kg dry weight, mean concentration data from Tables 8.1, 8.2 and 8.3*
*** *+ = upward (positive slope); – = downward; 0 = no significant difference or random pattern*

TABLE 8.7 Q TEST EVALUATION* OF MEAN FREON EXTRACTABLE CONCENTRATIONS**

Month	Study: Aerobic plus Nutrients	Anaerobic
0	58,900a	52,400a
1	55,200a	39,100b
2	61,400a	49,100a
3	35,800b	45,300a
4	46,300a	54,000a
5	———	45,900a
6	40,000a	———
8	38,600a	45,700a
Difference Pattern	0	0

* *means with a common letter in the same column and not significantly different (α = 0.05)*
** *mg/kg dry weight, mean concentration data from Table 8.4*
*** *0 – no significant difference or random pattern*

SECTION 9

PREDICTIVE MODELS FOR CLOSURE

INTRODUCTION

Both organics and metals accumulate at HWLT sites. An objective of this project was to determine whether existing models are appropriate for predicting or evaluating the changes in the persistence and mobility of the constituents in the accumulated residues at closure and during post-closure. The focus of this modeling effort was to evaluate a methodology for determining an appropriate closure option for a given site and not to choose an optimal closure option for all sites. The latter must be done on a case by case basis.

This modeling effort was conducted simultaneously with the sample characterization, spatial variability, weathering and degradation studies described in previous Sections. Ideally, the evaluation and use of the predictive models described in this Section should have occurred after data was available from the various laboratory studies. Such data could have been used with the models for a more focused evaluation of the models and more direct comparison of site data to model results.

This was not able to be done in this project because: (a) the respective models had to be evaluated and ultimately modified for use under closure and post-closure conditions since the models originally had not been developed for that purpose, (b) the modified models had to be checked to assure that results reasonable for closure conditions were being obtained, and (c) some of the laboratory results, particularly from the degradation studies, were not available until very late in the project.

Thus the input parameters to the models used in this evaluation were not those determined in the laboratory portion of this project. Rather, the input parameters and site specific scenarios used were those that were reasonable for petroleum refining and wood preserving wastes and for the land treatment of such wastes. The values for such parameters were obtained from peer reviewed literature and from studies in which land treatment had been used for similar wastes. The information provided in this Section and in Section 10 therefore does help meet the objectives identified earlier, i.e., to determine whether existing models are appropriate for identifying or evaluating changes in persistence and mobility of constituents in accumulated residues at closure and during post-closure of HWLT sites.

Greater details about this evaluation are available(34). The following information and discussion describes the models that were used, the modifications that were made in the models, and the model outputs and results that were obtained.

BACKGROUND

The Regulatory Investigative Treatment Zone (RITZ) model was used to evaluate the persistence and mobility of specific organic constituents. The MINTEQ model was used to evaluate the persistence and mobility of metals. To illustrate the use of such models for closure decisions, they were applied to a specific HWLT site, the Texaco site described in Section 3. Details about this site-specific application are presented in Section 10. The version of RITZ that was used was obtained from the Robert S. Kerr Environmental Research Laboratory (RSKERL), U.S. EPA, Ada, Oklahoma 74820, and the initial version of MINTEQ was obtained from the Center for Water Quality Modeling, U.S. EPA, Athens Environmental Research Laboratory, Athens, Georgia 30613.

Closure and post-closure plans must assure that soil conditions at HWLT sites are protective of human health and the environment. To accomplish this goal, there are a number of potential exposure pathways that must be considered. Contamination of groundwater is a major exposure pathway. Volatilization and contaminated dust emissions also can be of concern but the migration of contaminants to groundwater is the primary focus of this evaluation.

The activities described in this Section do not involve a traditional risk assessment in which a maximum exposure level is determined and an allowable residue concentration at closure is back calculated. Such studies have been conducted in related areas, such as active land treatment(35), and land disposal(36), and are useful in determining the quantities of the potentially hazardous constituents which may be applied in a particular scenario. However, at closure, accumulated waste residues already are present in the soil matrix. Therefore, an evaluation can begin with the concentration of the constituents as an initial condition, and estimate the mobility of such constituents under site specific conditions.

COMPUTER MODELS

There are many models available for examining the fate and transport of constituents in soil environments. However, presently there is not a single model which is able to adequately examine the mobility of both organics and inorganics in soils. In this evaluation, it was necessary to use separate models for organics and inorganics.

Several criteria helped determine the models used in this research. A major concern was availability. Models which are supported by the EPA or other major institutions, such as the United States Geological Survey (USGS), are readily available, and are periodically updated. Reports based upon the use of these models also are readily available from the sponsoring organization. Other concerns involved in choosing the appropriate model included applicability to HWLT and soil in general. All models are only as accurate as the assumptions behind them, and in the subsequent parts of this section, the assumptions that are part of the models used are noted.

Organics

The model used in this research for organics was the RITZ model(37), which was developed at the EPA Robert S. Kerr laboratory in Ada, Oklahoma, based upon the earlier work of Jury et al.(38). This model has been used to describe the fate of organics in HWLT(5) and has been improved several times since its creation(39-41). A full discussion of the background and mathematics of RITZ is beyond the scope of this report and is available in the above citations.

The structure of RITZ is straightforward. A mass balance is calculated in the ZOI for the applied waste. The concentration of the organic constituents in solution are modified by the treatment processes that occur in the soil. The remaining mass is then leached into the LTZ, where another mass balance is calculated. Any mass still remaining in solution can leach from the bottom of the LTZ, where it can present a threat to groundwater.

There are many limitations to the RITZ model. An obvious source of error is the uncertainty in the existing data. For most organics of concern, the parameters associated with the treatment processes are often unavailable. Many of the partition coefficients are simply estimates obtained from octanol-water partition coefficients. Half-life data also are scarce.

A study conducted by the American Petroleum Institute(5) demonstrated that the RITZ model is highly sensitive to the loading rate and the degradation rate. This is fortunate because it makes the uncertainty present in the available data for the partition coefficients less critical in examining HWLT scenarios.

There also are limitations built into the assumptions of the RITZ model. One is the assumption of a constant infiltration rate. In reality, rainfall occurs sporadically, and the infiltration is not uniform. In a managed site, with irrigation, the infiltration can be more uniform. Other simplifying assumptions in RITZ involved in the mathematical derivation are noted later in this Section.

Inorganics

All of the models available for inorganics are aqueous equilibria models. In such models, the concentrations of the various constituents in an aqueous solution are input to the model. These concentrations are usually the total concentration of a given component in the solution, such as total calcium. The model then calculates the speciation, or the form in which the components are found in the solution. For example, calcium will often be found in solution as $CaCO_3$. These models are very useful because it is much easier to measure the total concentration of a given element than it is to measure the concentration of all the forms in which it is found in solution. In a normal soil solution, there may be many different solution phase forms of an element.

The model used in this research for metals was MINTEQ(42). As with RITZ, it is a model supported by the EPA and has been demonstrated to be applicable to the analysis of migration potential in subsurface soils(36). MINTEQ was developed using a combination of the better features of two other models, MINEQL(43) and WATEQ(44). A major advantage of MINTEQ is its maintenance by the EPA, which allows its thermodynamic database to be updated regularly.

MINTEQ, like all aqueous equilibria models has a major drawback, in that it is only an equilibrium model and is not able to examine kinetics. Natural systems are very rarely, if ever, at equilibrium. There is very little known about the kinetics of natural systems, and the equilibrium assumption is necessary. The other limitations are those inherent in the assumptions which are used throughout the derivation of the model, as well as in preparing the input data. MINTEQ output cannot provide the actual soluble concentration of a given metal, but can demonstrate potential problems with soluble metals.

As with RITZ, a major drawback to MINTEQ is the available data. The number of possible reactions involving the inorganic constituents in a soil solution is extremely large and the available data is applicable to only a fraction of these. Usually, the major reactions are described, and the error introduced by ignoring the other reactions is minimal. However, in soils there may exist some species which are not adequately described by the existing thermodynamic data, such as metal-clay complexes.

CLOSURE OPTION SITE IMPACTS

There are a number of closure options available for a HWLT site or a site with contaminated soil (Table 1.1). The key point in selecting an appropriate method for a site is the extent to which the migration potential of the accumulated potentially hazardous constituents is reduced. If a low migration potential is predicted with models or laboratory studies, the site could be left alone. At a site with an excessive migration potential, it might be necessary to remove the contaminated soil.

Each option will result in changes to the conditions at the site during the post-closure period (Table 1.2). It is important to consider the changes which are likely to occur at the site after the options are implemented.

Removal of Contaminated Soil

With this option there is little need to examine the changing site conditions over time. This option will only be necessary if the results of the computer modeling or laboratory or field studies show that the potential threat for a given constituent to migrate is large, and that this threat is not likely to be prevented by other closure options. At some sites, only part of the contaminated soil may be removed, that with the greatest potential for migration. This could cause changes in the remaining soil, which may still contain some potentially hazardous constituents.

The soil under that which is removed will have an increase in available oxygen due to diffusion from the atmosphere. This will promote aerobic degradation and is likely to create an oxidizing environment. The remaining site soil must be regraded in order to maintain the run-on and run-off requirements. This will cause mixing, and possibly some dilution of the contaminated soil. The physical process of regrading will induce some additional volatilization, as more organic constituents will be exposed to the atmosphere.

Capping a Site

There can be differences in site conditions due to the use of impermeable and vegetative caps. With a cap of permeable soil that can support vegetation, there may be only moderate changes. For example, if the pH had been maintained at over 6.5, discontinuation of this management practice may result in a gradual decrease in pH. With only moderate tilling, the oxygen diffusion rate may decrease and there may be a less uniform infiltration rate.

With a clay cap, other changes may occur. Reduced gas diffusion through the cap may increase the partial pressure of carbon dioxide in the soil resulting in less oxygen in the soil pores. As a result, aerobic biodegradation processes may be diminished. With the decrease in the oxygen content of the soil, redox conditions will become reducing which will affect metal solubility.

Capping also will reduce the infiltration rate and will prevent the leaching of constituents in the accumulated residue. However, with the change to anaerobic conditions, the degradation of these organics will not proceed as rapidly, and constituents will remain in the site longer. After the post-closure period, the land at the site may be opened for other uses. There is the possibility that constituents remaining in the site when it is opened could present a hazard at that time. Therefore, it is important when looking at the use of a clay cap to consider the amounts of the residues which will remain for long time periods.

Leave Site Alone

In terms of the possible changes occurring over time, this option is very similar to the vegetative cap. There may be a decrease in the gas diffusion into and out of the soil, and an associated decline in the aerobic degradation rate.

Continued In-Situ Treatment

This is the simplest case to model. There should only be gradual changes to the site conditions. For example, with the cessation of the waste application, there could be a decrease in the number of bacteria which are dependent upon a certain waste constituent as their main substrate, and an associated drop in the overall degradation rate.

MODEL MODIFICATIONS

RITZ

The RITZ model is a fate and transport model, and the use of RITZ for examining the movement of organics through the soil at HWLT sites is straightforward. The version of RITZ obtained from RSKERL was modified for this research. The modifications included: (a) considering that the degradation rate will vary and decrease with time and with increasing depth from the soil surface, (b) the existence of a separate oil phase in the soil, the separate degradation of the oil phase and that some of the constituents may partition into the oil phase and move with it, (c) allowing different oil degradation rates in the ZOI and LTZ, and (d) having different values of the chemical partition coefficient in the ZOI and LTZ as recognition of the different organic matter content as a function of depth in these zones. In addition, the model was modified to function with no waste input to the ZOI. Only those constituents that were considered to exist at closure were to be evaluated.

An assumption of the early RITZ model was that of a constant degradation rate throughout the treatment zone over both time and depth. In reality, the degradation rate will vary. The degradation rate is dependent on such factors as microbial population density, oxygen and substrate availability, as well as temperature. During the active site life, the degradation rate will depend more on depth than time, since the major variables will be microbial population density and oxygen diffusion, both of which will cause the degradation rate to decrease considerably with depth. The variability with time, however, can become important after closure. For example, when no further substrate is applied, or in the case of a clay cap being placed over the site, the degradation rate could change. In the case of a clay cap, the buildup of carbon dioxide could change the conditions at the site from aerobic to anaerobic. Most of the degradation rates of the organics of concern are slower under anaerobic conditions(45). For this evaluation, the following expression was utilized in order to allow the degradation rate constant to vary with both time and depth:

$$\mu = A \exp(-\omega t - \gamma z) + B \tag{9.1}$$

where: μ is the first-order degradation rate constant, ω is the degradation rate time constant, γ is the degradation rate depth constant, and A,B are constants. The depth, z, can be related to time, t, by:

$$z = \frac{Vt}{R} \tag{9.2}$$

where: V is the Darcy velocity and R is the retardation factor. The Darcy velocity is the annual infiltration rate converted into the units of meters/day. The retardation rate is calculated by:

$$R = \frac{\rho K_D + \theta + \eta K_H + \phi K_o}{\theta} \tag{9.3}$$

where: ρ is the bulk density of the soil, θ is the volumetric water content of the soil, η is the volumetric air content of the soil, and ϕ is the volumetric oil content of the soil. The volumetric oil content of the soil also is modified throughout the calculations by considering the first order degradation of the oil phase:

$$\phi = \phi_{\text{initial}} \exp(-\mu_0 t) \tag{9.4}$$

where: μ_0 is the degradation rate constant for the oil phase.

The previous relation for depth as a function of time is only valid when the retardation rate is not a function of time. At closure, the volatile fraction of the organics is usually assumed to be negligible. Furthermore, the rapidly degrading oil phase has already disappeared. Therefore, at closure it can be assumed that the retardation factor is not a function of time. As with the constituent rate constant, the degradation rate constant for the oil phase also is considered a constant in the RITZ model. One modification used in this research was the varying of the oil phase degradation rate between the ZOI and the LTZ. A default value was chosen in which the oil phase degradation rate constant in the LTZ was set equal to 10% of the degradation rate constant in the ZOI.

This new degradation rate constant was inserted into the expression for the mass remaining: $\frac{dm}{dt} = \mu t$ and integrated. The following expression was obtained:

$$M = M_0 \exp\{(\frac{AR}{R\gamma + \omega V}) [\exp(\frac{-\gamma R - \omega V}{R})t - 1] - Bt\} \tag{9.5}$$

Upon the use of the boundary conditions, it can be shown that: $A = \mu_0 - \mu_\infty$ and $B = \mu_\infty$ where μ_0 and μ_∞ are the initial and final degradation rate constants, respectively.

This modified degradation rate constant was used in the RITZ model. Unfortunately, these are simply two more constants for which little data are available. A value for γ of 3 m^{-1} has been reported(46). The value for ω can be regarded more as a sensitivity tool, than an actual measurement. In the case of capping a site, the degradation rate would be expected to decline more rapidly than with the other closure options, and the sensitivity of the RITZ model to the changing degradation rate can be examined by varying the ω parameter. The default values in the computer code for both ω and γ are 0, which will cause the degradation rate constant to be equal to its initial value.

Another modification involved the calculation of the soil:water partition coefficient, K_D. This parameter can be calculated based upon the fraction of organic carbon (f_{oc}) present in the soil. In RITZ, one value for the f_{oc} is input, and is used throughout the depth of the treatment zone. However, at most land treatment sites, there is a higher organic matter and organic carbon content in the ZOI. This difference is even greater at land treatment sites where organic residues have accumulated in the surface soil. An important change was made to RITZ to allow the input of two different values for the f_{oc}, one for the ZOI, and one for the LTZ. If an organic is able to pass through the top layers of the soil, there will be much less organic matter to retain it at lower depths, and the potential for its continued migration to the groundwater is greater.

There is another facet which must be discussed in order to better understand the output of the model. The constituent of interest is modeled as a slug moving in plug flow through the soil profile. Therefore, there will exist upper and lower boundaries outside of which the constituent is not found in the soil water. The zone above the slug, the zone through which the constituent has already passed is defined as the "dry" zone, and the area with the constituent is defined as the "wet" zone(47). The constituent may be found in the dry zone as it volatilizes and moves through the soil air. This is a simplifying assumption. In reality, organic constituents may adsorb onto the soil, and desorb into the "clean" water above the pollutant slug. These concentrations will be much lower than those in the pollutant slug. It is the pollutant slug which is acted upon by the treatment processes, such as partitioning and degradation.

MINTEQ

MINTEQ is an aqueous equilibria model, and not a fate and transport model. Since equilibrium models are all that are available, methodologies have been developed by which these models can give some insight into the mobility of inorganics in natural systems.

This is done by examining the solubility of the inorganics, in this case metals. Since only the aqueous phase of the soil is mobile, the potential for migration of the inorganics can be limited to only those which are soluble. MINTEQ can examine a soil solution, and determine the fraction of each inorganic which remains soluble. In the worst case scenario, all of the metal which is soluble will migrate. Therefore, by examining the concentrations of the soluble metals in the soil solution, the metals most likely to migrate can be determined.

The version of MINTEQ used in this research was developed at the EPA laboratory in Athens, Georgia(42), and was installed in a Micro-Vax computer at The University of Texas. Unlike RITZ, MINTEQ was not modified for this research. Several minor changes were made to facilitate the input and output and these are discussed later in this Section.

MODEL INPUTS AND OUTPUTS

RITZ

RITZ can only model one organic at a time. Therefore, modeling a complicated waste requires many runs to examine various organic constituents.

The first input data which RITZ requires are the soil data. The actual parameters required are: (a) saturated hydraulic conductivity, K_s, (b) residual moisture content, θ_r, (c) Brooks and Corey exponent parameter, ε, (d) fraction of organic carbon in the ZOI, ($f_{oc,ZOI}$), (e) fraction of organic carbon in the LTZ, ($f_{oc,LTZ}$), and (f) soil porosity. The first three are all related to the Brooks and Corey model for moisture infiltration in soil(34,35). They are not usually included in the site data, but can be estimated based upon the soil textural classification. These classifications, such as clay or silty loam, can either be included in the site permit application, or can be determined based upon soil surveys conducted at the site. Soil surveys are generally available on a county wide scale. Table 9.1 contains average values of these parameters for most of the soil types of interest.

The next two parameters are obtained directly from the soil core measurements which have been taken previous to closure as part of the waste residue characterization. Most sites show a large decline in organic carbon with depth. These values can be used in several ways. One is to take the actual core measurements for a given plot and use those numbers to model all the constituents in that plot. However, this will involve a large number of model runs. A simpler method is to take average values of these parameters for the entire site, and run all the constituents with these values. In addition, worst case parameter runs also can be made. This results in only two runs for each constituent. If the worst case run shows the potential for contamination, subsequent plot specific runs can be made to focus upon the potential threats. The soil porosity can be obtained from the soil core measurements, or estimated based upon the textural classification of the soil at the site.

The next input data required are the atmospheric and hydrologic parameters: (a) mean annual temperature, °C, (b) mean annual relative humidity, %, (c) annual infiltration rate, m/yr, and (d) daily evaporation rate, mm/day. Data for several of these parameters may be available in the permit application. If not, they can be estimated from various sources. Contour maps are available(48) which show the average rainfall, temperature and evaporation data for the various regions in the United States. These data often are available from local sources.

When modeling an actual site, water balance calculations can be used to estimate the net infiltration at the site. This estimate is of great importance to the mobility of contaminants in soils and should be as accurate as possible.

TABLE 9.1 BROOKS AND COREY PARAMETERS USED IN RITZ
(Adapted from Reference 49)

Soil Texture	Porosity	θ_r	Ks(cm/hr)	ε
Sand	0.349	0.017	30.23	6.7
Loamy Sand	0.410	0.024	79.10	7.5
Sandy Loam	0.423	0.048	18.93	8.3
Loam	0.452	0.034	6.52	11.1
Silt Loam	0.484	0.018	1.64	12.7
Sandy Clay Loam	0.406	0.075	4.94	8.8
Clay Loam	0.476	0.087	3.84	10.7
Silty Clay Loam	0.473	0.054	1.13	15.2
Silty Loam	0.476	0.085	2.36	13.8
Clay	0.475	0.106	1.19	13.7

The evaporation and humidity data are used by the model to calculate volatilization losses and a water balance. The annual infiltration rate is important to a water balance. The RITZ model can be manipulated to examine the sensitivity of changing the infiltration rate.

The next set of data is that directly related to the waste application: (a) time between waste loadings, days, (b) volume oil per unit area in ZOI, (cm^3/cm^2) cm, (c) waste chemical mass application to ZOI, g/m^2, and (d) number of simulated waste loadings. At closure, these values can be determined easily. Since there will be no further waste loadings, the number of simulated loadings is 1 and the time between waste loadings is the time of the simulation. The RITZ model will compare the input time between waste loadings with the time it calculates for the mass to remain in the ZOI. RITZ will take the shorter of the two times and output a profile of the constituent mobility in the ZOI for this length of time.

Therefore, in modeling closure, time during the post-closure period can be varied to estimate the mobility of an organic in the ZOI and LTZ. The volume of oil in the ZOI can be determined from the soil core data. The values for the oil volume, cm, are obtained by dividing the volume of oil applied, cm^3, by the area to which it is applied, cm^2. The mass of a contaminant can be obtained by using the soil core data for the concentration of a given constituent in the ZOI, and then calculating the applied mass. For the purpose of this research, the computer code of RITZ was modified to allow the input of an initial ZOI concentration. This technique is much simpler to use in modeling closure, since this concentration is known. However, in the modeling of active HWLT, it is the pollutant mass applied which is known.

The last group of input data for RITZ is that relating directly to the various organic constituents: (a) organic carbon partition coefficient, K_{oc}, (b) Henry's Law constant, K_H, (c) water-oil partition coefficient, K_o, (d) initial constituent half-life, $t_{\frac{1}{2},0}$, days, (e) final constituent half-life, $t_{\frac{1}{2},\infty}$, days, (f) oil phase half-life, $t_{\frac{1}{2},oil}$, days, (g) degradation rate time constant, ω, $days^{-1}$, and (h) degradation rate depth constant, γ, m^{-1}. The values for the partition coefficients and the degradation rates are available in the literature. For the degradation rate depth constant, a value can be estimated based upon records of microbial activity versus depth. The time constant is not available, but as discussed previously, this parameter can be varied to investigate the sensitivity of the migration potential to the various closure options. Another minor modification of RITZ for this evaluation was to decrease the degradation rate of the oil phase in the LTZ to 10% of the rate in the ZOI. For the relatively small amount of the oil phase remaining at closure this assumption is likely to produce little error. A similar technique has been used(39) in the development of the RITZE, or enhanced RITZ model.

The version of RITZ used in this research was written in BASIC, and run on an IBM PC, or an IBM compatible machine. The input was done interactively. With the inputs identified, the output from RITZ can be examined. The first section of the output is an echo of the input parameters. The soil and hydrologic information, such as porosity and infiltration rates, are repeated as are the organic constituent characteristics, such as partition coefficients. An initial constituent concentration in the ZOI, as well as an initial retardation factor are calculated.

The next section of the output concerns the ZOI. The time that a given constituent spends in the ZOI is calculated. This is the time it will take for the upper boundary of the pollutant slug to pass through the 0.15 m depth of the ZOI. The time of the simulation is then separated into a series of intervals. For each interval, the depth of the top and bottom of the slug, the "dry depth" and "wet depth," are calculated. The amount of volatilization, as well as the amount of the organic leached, and the concentration of the leachate are calculated. Finally, the cumulative totals for leaching, volatilization and degradation are calculated. The residual mass, that mass which has not volatilized, degraded or leached also is calculated. Therefore, the amount of a given organic remaining in the ZOI at a given time is known.

Similar calculations are then made for the mass of the organic constituent which has leached into the LTZ. A time is calculated for the pollutant slug to move entirely through the 1.5 meter treatment zone. The only values reported for the LTZ are the leaching data. The volatilization of an organic from the LTZ is negligible. The most important aspect of this output is the cumulative leachate. This demonstrates the amount of mass, if any, of the given organic constituent which has migrated out of the treatment zone and into a depth where it may pose a threat to groundwater.

The final section of the output is a summary of the fate of the given constituent. The complete mass balance is given for both the ZOI and LTZ. The mass of the constituent remaining in the treatment site at the end of the simulation also is shown, as is the time for the organic constituent to pass through the LTZ.

MINTEQ

The inputs to MINTEQ are far more complicated than those to RITZ. Fortunately, a preprocessor code, PRODEFA1 has been developed which allows for the interactive preparation of the MINTEQ input file. A users guide for MINTEQ is available(42), and the documentation for the PRODEFA1 is available on distribution diskettes. The actual structure of the input file is not important, but what is important is the development of the data which is included in the input file.

MINTEQ is used to model the aqueous phase, or soil solution, as it moves through the soil profile. The best input to MINTEQ would be an actual analysis of the soil solution at a given site. Unfortunately, this analysis is difficult in practice, and is only infrequently available. Therefore, various approximations must be used. It is important to remember how the model is used. Measured concentrations of the various elemental and ionic components are input, and the model calculates the form in which these ions actually exist in solution at equilibrium, i.e., the speciation. For example, the concentration of Fe^{+3} can be measured, but in solution, Fe^{+3} will exist in many forms, such as $FeOH_3$, $FeOH_2^-$ and even the free ion Fe^{+3}. It very difficult to measure the actual amount of each form of iron in solution, and only values for the total iron are reported. This is even more true when redox equilibria are involved. It is much simpler to measure the total metal and impose the redox conditions of the solution on the metal to estimate its speciation, than it is to accurately measure the concentrations of all the redox states of the metal.

An important distinction must be made between soil solution metals and total metals in the soil. Soil solution compositions are infrequently measured, while soil total metals are commonly measured. The values for total metals need to be evaluated carefully. High values will be reported for certain metals, such as iron and aluminum. This is due to the elemental composition of the soil minerals, and not the applied waste.

There are several key variables which influence metal solubility in the soil. The major ones are pH, and redox state. Another is the gases with which the system is in equilibrium. In a site open to the atmosphere, the dominant gas is oxygen, while in a capped site, or deep in the soil profile, the dominant gas is often CO_2. Not only will these gases influence redox conditions, they also will influence the speciation by forming different complexes with the metals present in the solution.

Various approximations are made in order to model the soil solution at HWLT sites. The first is the substitution of a generic soil solution. The pre-application soil solution is a product of the equilibria between the soil minerals, the biological fraction, the soil water and the atmosphere. The major variables affecting the soil solution composition are the pH and the mineral composition of the soil. The next step is to impose the site conditions upon the composition of the soil solution to obtain the speciation which would be found at the site. One complication is the presence of natural organics in the soil solution. These organics are both short chain ligands, or long chain compounds often referred to as "humic" or "fulvic" acids. These acids are not individual compounds, but rather a variety of compounds inherent in the soil organic fraction. MINTEQ does not contain many of these organics in its current database, but does contain several generic ligands which can be used to simulate these organics, both the long and short chain types. Since the fraction of organic carbon in soils varies, these inputs must be varied from site to site.

There are other difficulties present in using this approximation, and in modeling inorganics in general. The difficulty in measuring redox conditions, pE, in natural systems has been well documented(50). Furthermore, the ability of the existing models to handle redox equilibria is limited. The databases are small, and the reliability of these data in natural systems is largely unknown. The best way to examine redox problems in soil systems is to examine the effects changes in redox conditions will have on the metal equilibria. It is possible to determine whether a soil is in oxidizing or reducing conditions, and then to examine the results of changes in this status.

The next complication to consider is the form of the applied metal. In a waste solution, a metal will be in many forms. To successfully model metal mobility, these forms must be known. An important parameter in examining the input metals is the amount of the metals which are complexed by organics. Metals complexed by organics may not be subject to the same equilibria as those existing in ionic forms. If the organic complex is insoluble, there will be less soluble metals than that predicted by the model. However, if the organic complex is soluble, the soluble metal concentration could be underestimated. In a simple aqueous waste, a full analysis can be done on the waste, and these results used as input into MINTEQ in order to determine the speciation of the waste stream. This speciation can then be used in conjunction with the modeling of the metals in the soil to examine solubility. In complicated waste streams, such as refinery wastes with large amounts of organics, it is very difficult to determine the forms of the applied metals.

Another consideration in determining the form of the metal in the waste stream is the redox state of the input metal. An example is chromium. In its oxidized state, Cr^{+6}, chromium exists in solution as CrO_4^-, and is far more mobile than the reduced form of the metal, Cr^{+3}. Therefore, not knowing the form of chromium in the waste could lead to underestimating its mobility.

The last major assumption is that of equilibrium. Natural systems are very rarely, if ever at total equilibrium. Fortunately, natural systems usually approach equilibrium.

There are several minor assumptions needed in using MINTEQ. The first is that of constant temperature, usually chosen as 20 or 25°C. Within the range of temperatures found at HWLT sites, this assumption will lead to minimal error. Most of the other assumptions are related to the calculation of ion activity and activity coefficients. The various methods for calculating activity coefficients, such as the Davies method, or the Debye-Huckel method, are all approximations, but they are the best available at this time.

Once an input data set which adequately describes the HWLT site soil solution has been developed, the next important step is entering the input data. The code, PRODEFA1, developed to create the input file, uses an interactive technique to prompt the user for the input data necessary to run the program. Most of the information necessary to use this code is available in the help files which are distributed with the code.

MINTEQ output is quite lengthy, and must be analyzed in detail to obtain the information important to evaluating the potential mobility of constituents at HWLT or closed sites. As with RITZ, the first section of output echoes the input file. The next output is called "Input Data Before Type Modifications" which is a repeat of the input data in a slightly different form. The next output is the unspeciated charge balance. This is important because it provides a measure of the quality of the water analysis. All solutions must be charge balanced, and a large error in this value means that the analysis is incorrect, or incomplete. MINTEQ has an option to abort the calculation if the charge balance error is greater than 20%. If the calculation is aborted, it is important to verify the input concentrations.

After the charge balance, MINTEQ begins the actual calculation steps. One component is selected for each iteration and examined by MINTEQ to see if the convergence criteria are met. The criteria are described in the MINTEQ manual(46). Throughout the calculations, MINTEQ keeps track of all the minerals which precipitate or dissolve. One potential difficulty to the calculations is the violation of the phase rule. This occurs when too many minerals control the solubility of a given element. For example, calcium can not be in simultaneous equilibrium with calcite, kaolinite and calcium nontronite. When MINTEQ calculates that all three of these precipitate, it will create a phase rule violation and abort the calculations. In reality, all three of these minerals may be present in a soil system. Nature can bypass the phase rule by existing out of equilibrium, or one mineral can dominate the system. The phase rule is followed by various local equilibria throughout the heterogeneous soil solution. In using MINTEQ, it is sometimes necessary to not allow a given solid to form in order not to violate the phase rule.

After the convergence criteria have been met, MINTEQ begins the output data. This begins by stating output data, and the number of iterations it took to arrive at this step. The first block of output is an accounting of the input elements and ions. This is mainly an indication of what amount of the input element remains in the same form after the speciation.

The next block of output is what MINTEQ refers to as the Type I components. These are the "master solution species," or the species in which the given elements usually are found in solution. For sodium, this form is Na^{+1}, while for silica it is H_4SiO_4. The next output are the Type II complexes. This is a listing of all the different ionic complexes formed by the input constituents. It is important to note that these are all soluble complexes. Next comes the Type III, or fixed solids. These are not always solids, but can contain any species which is fixed by the user as invariant. For example, water is almost always a fixed solid. Also, if the pH is set as invariant, the hydrogen ion is also a fixed solid. There are two other important examples. First, it is often necessary to fix the partial pressure of CO_2 gas in equilibrium with the system, as is the case in any system which is open to the atmosphere. When this is done, the partial pressure of CO_2 becomes a fixed solid. Another example involves redox equilibria. When a pE is specified, all the redox pairs, such as Fe^{+2}/Fe^{+3}, are specified, and these ratios are then fixed solids. Sometimes the pE can be specified by fixing a redox pair, and MINTEQ will calculate the pE from this pair.

The next two sections of output describe the various mineral phases in equilibria with the soil solution. The Type IV group are the precipitated, or insoluble minerals. The Type V solids are those which are dissolved, and are found in solution. The last group, Type VI, are those species not included in the calculations. These include those minerals left out by the user in order not to violate the phase rule, as well as other species MINTEQ does not include for other reasons, usually relating to redox conditions, or to gaseous elements not described by the user as being in equilibrium with the system.

The next section is one of the most useful in examining the solubility of a given species. This helps to simplify the examination of all the output data. A given element could be listed in 12 different species, but 99.9% of that element could be in only one species. By only looking at the species which contain a significant amount of the soluble metal, even 1%, the number of species to be examined can be diminished greatly. The fraction of metal which is soluble can be obtained by comparing the species indicated by this section of output to the input concentration. The next output section is also useful. This states the aqueous and sorbed masses of the input constituents. Again, the fraction of input metal remaining soluble can be obtained by comparing the aqueous mass to the input mass.

MINTEQ next repeats the charge balance calculations for the speciated solution. This will usually not vary greatly from the unspeciated charge balance. The last section is the saturation indices for all the solids present. This is an indication of how close the solution is to the saturation point, or the point at which the mineral will precipitate. A negative saturation index indicates undersaturation, while a positive value indicates supersaturation. If the value is zero, the mineral has precipitated, and the solution is in equilibrium with this mineral. An actual measured solution can often be supersaturated with respect to a given mineral, but MINTEQ will not allow this to occur in the calculations. This is another manner in which natural systems can bypass the phase rule.

When MINTEQ models natural systems, the concentration of the given elements are used to calculate the speciation which would be found if the system were in equilibrium. Unfortunately, due to the various approximations inherent to the model, as well as the limitations in knowledge of natural systems, these values are not entirely accurate. These values should be regarded as indications of potential problems with metal mobility, and not as actual values of soluble metal concentrations. In other words, a metal which MINTEQ shows to remain 100% soluble is likely to be mobile, while a metal which remains only 0.1% soluble is much less likely to be mobile.

SENSITIVITY TO PARAMETERS INFLUENCED BY CLOSURE

There are a number of site parameters which will be influenced by closure. Therefore, in examining a closure option, it is important to have an understanding of the influence these changes will have on the mobility of the constituents present at the site. An analysis was conducted to examine the influence that these changes had on the results of the RITZ and MINTEQ models.

RITZ

In this analysis, the most important variables examined were the degradation rate depth and time constants. An API study(5) examined the use of RITZ to model an active HWLT situation and the sensitivity of RITZ to parameters associated with HWLT.

The results of the API analysis indicated that the only parameters which had any effect on the persistence of the organics were the degradation rate and the initial concentration in the ZOI. This was easily explained. The longer the half-life, the longer it takes a given mass of organic to degrade. Furthermore, if the initial mass was greater, the amount remaining at a given time would be greater, even though the fraction of mass remaining would be the same.

The RITZ model was sensitive to the site parameters that affect the mobility of the organics. The soil/water and oil/water partition coefficients, K_D and K_O, had some effect on organic mobility. This was especially true for compounds which had lower values for these parameters as well as relatively long half-lives. Compounds with high K_D and K_O values were retained in the ZOI long enough to degrade, and compounds with short half-lives degraded before they could migrate.

These results are important for closure for several reasons. First, at closure the concentration of constituents in the soil can be known fairly accurately. Soil core analyses determine the concentration of each constituent present. Any lag time between the taking of the soil cores and initiating closure will only cause a decrease in the amount of the organics present. The degradation rate is not well known, but ranges of values have been reported for most of the constituents of interest. The infiltration rate is variable, but estimates can be made based upon the climate of the site or from actual site measurements.

Several parameters that were not included in the API analyses were included in this analysis: the initial oil content of the site and temperature. In examining the initial oil content of the soil, the sensitivity of the model to the oil decay rate also was examined.

Temperature and Relative Humidity - It was important to demonstrate the sensitivity of the RITZ model to temperature and relative humidity, since these vary at a site over a year. The soil types used in this analysis of temperature and relative humidity effects were a sandy loam, a clayey loam, and a sand. The parameters for these soil types were noted in Table 9.1. The organic chosen for this evaluation was naphthalene, since this was the most sensitive of the compounds used in the API analysis. The partition coefficients and degradation rate for naphthalene were chosen from the range of values tabulated in the API report. The f_{oc} was chosen to be 0.028 in the ZOI, and 0.010 in the LTZ. Both of these are at the low end of values at a HWLT site that has been operating for some time (Section 6). The initial oil volume was 1.5 cm^3 of oil per cm^2 of soil (1.5 cm). The initial organic concentration was 500 g/m^3. Table 9.2 summarizes the parameter values used in this analysis. In examining the temperature variation, the relative humidity was set to 50%, and in examining the relative humidity variation, the temperature was set to 14°C. The infiltration was 0.85 m/yr, and the evaporation was 1.2 mm/d. This value for the infiltration is quite high, and was meant to simulate a time period of excessive precipitation.

TABLE 9.2 PARAMETER VALUES USED IN EXAMINING RITZ SENSITIVITY TO TEMPERATURE AND RELATIVE HUMIDITY

Parameter	Value	Parameter	Value	
Infiltration	0.85 m/yr	Evaporation rate	1.2	mm/d
$f_{oc,ZOI}$	0.028	$f_{oc,LTZ}$	0.010	
Initial oil content	1.5 cm	Initial concentration	500	g/m^3
log K_{oc}	3.0	K_H	0.3	
K_O	170	$t_{1/2}$	20	d

A range of average temperatures was selected to encompass the values observed at HWLT sites throughout the United States. However, for this example (Table 9.3), RITZ was not sensitive to temperature. The percent volatilized changed by at most 0.10 across the range, in the case of the sand, and the percent degraded changed by at most 0.02. The amount leached, which is the primary concern in HWLT, did not change for any of the soil types.

TABLE 9.3 SENSITIVITY OF NAPHTHALENE LOSS TO TEMPERATURE VARIATIONS

Soil Texture	Temp. (°C)	% Degraded in ZOI	% Volatilized from ZOI	% Leached from ZOI
Sandy loam	5	94.51	2.83	0.84
Sandy loam	10	94.52	2.85	0.84
Sandy loam	15	94.52	2.86	0.84
Sandy loam	20	94.53	2.89	0.84
Clayey loam	5	94.34	2.90	0.90
Clayey loam	10	94.34	2.90	0.90
Clayey loam	15	94.34	2.90	0.90
Clayey loam	20	94.34	2.91	0.90
Sand	5	79.64	9.74	0.76
Sand	10	79.64	9.76	0.76
Sand	15	79.65	9.79	0.76
Sand	20	79.66	9.84	0.76

The RITZ model also demonstrated little sensitivity to relative humidity. The values selected, 10%, 50%, and 90%, cover a reasonable range of values that may be encountered in various locations in the United States. As can be seen in Table 9.4, the amount leached (migrated) from the ZOI also was unaffected by the relative humidity value, although there were some minor variations in the percent degraded and the percent volatilized. The sum of the percentages in Tables 9.3 and 9.4 does not total 100%. There is a small mass balance error associated with RITZ. The primary factors causing such a difference are: (a) there is some round-off error associated with the calculations and (b) it is difficult to approximate the volatile losses of compounds with very high Henry's Law coefficients.

The differences between the various soil types for the parameters of concern were very small. The major differences were in the fate of the organics, with much more degrading in the sandy loam and clayey loam than in the sand. However, the amount volatilized in the sand was greater. The percent leached was basically unaffected with the value only changed by 0.14% (Table 9.4).

TABLE 9.4 SENSITIVITY OF NAPHTHALENE LOSS TO RELATIVE HUMIDITY VARIATIONS

Soil Texture	Relative Humidity	% Degraded in ZOI	% Volatilized from ZOI	% Leached from ZOI
Sandy loam	10%	94.53	2.92	0.84
Sandy loam	50%	94.52	2.86	0.84
Sandy loam	90%	94.51	2.81	0.84
Clayey loam	10%	94.35	2.91	0.90
Clayey loam	50%	94.34	2.90	0.90
Clayey loam	90%	94.34	2.90	0.90
Sand	10%	79.67	9.89	0.76
Sand	50%	79.65	9.79	0.76
Sand	90%	79.63	9.68	0.76

There was no sensitivity to either temperature or to relative humidity within the ranges evaluated. The mobility of organics was unaffected by these parameters, since the percentage leached to the LTZ did not change when any of the variables were changed. The persistence was also unaffected. Persistence was defined as the time a given organic compound remained in the ZOI. The API study demonstrated that the persistence is only affected by the degradation rate and the initial concentration, neither of which are altered in RITZ by the temperature and relative humidity. In reality, the microbial degradation rate is a function of temperature. In RITZ, the temperature used is an average annual temperature, and over the course of a year the temperature fluctuations will create an average degradation rate. At a HWLT site the degradation rate will be greater than the average value in the summer, and less in the winter.

Oil Phase Parameters - In examining the sensitivity of RITZ to the oil phase parameters, the following soil types were used: loamy sand, sandy loam and sandy clay loam. Table 9.1 contains the soil parameters used for these soil types. The organics evaluated were naphthalene, phenanthrene and chrysene. Table 9.5 contains the partition coefficients and half-lives for these organics. The temperature was set to 14°C, and the relative humidity to 50%. The infiltration was 1.0 m/yr, and the initial concentration was set at 500 g/m^3. The f_{oc} was 0.028 and 0.010 in the ZOI and LTZ, respectively. The time of simulation was one year. This time was long enough for most of the applied organic to degrade, but was still short enough to demonstrate some of the differences created by the range of half-lives and partition coefficients of the constituents.

TABLE 9.5 FATE AND TRANSPORT PARAMETERS USED IN ANALYSIS OF OIL PHASE PARAMETERS (Adapted from Reference 5)

Organic Constituent	log K_{oc}	K_H	K_O	$t_{1/2}$ (days)
naphthalene	3.0	0.3	170	20
phenanthrene	4.13	0.004	1950	45
chrysene	4.35	0	2000	60

The initial oil volumes examined, expressed as depth of oil over an area in the model (cm^3/cm^2), were 0.2, 1.5 and 3.0 cm. These values simulate the range expected at a HWLT site. The highest value, 3.0 cm, would simulate the oil content soon after application, before the rapidly degrading portion disappears, while the low value, 0.2 cm, would simulate the residual oil content well after application. The oil phase half-lives examined were 35 and 350 days.

The oil decay rate and the soil type had very little effect on the mobility and persistence of the applied organics. Results for the loamy sand are presented in Table 9.6. Similar trends were demonstrated for the sandy loam. The sandy clay loam had similar results for the 0.2 and 1.5 cm initial oil contents, but became oil saturated with the 3.0 cm application. At an actual site, it is likely that a large application of oil will be readily apparent to the site operators, and future applications would be decreased so as not to oil saturate the soil.

The sensitivity of RITZ to the oil phase parameters was most apparent for naphthalene. This may be due to its volatility. With less oil in the soil, due to either a greater oil decay rate, or to less initial oil volume, there is more organic in the water phase, and therefore more which can partition into the air phase, or more that can be degraded. Naphthalene has the highest Henry's Law constant, and its fate is more dependent on the amount of constituent in the water phase.

In terms of the modeling, the choice of a rapid decay rate for the oil phase, such as a 35 day half-life, resulted in a worst case scenario being modeled. Since the oil phase is simply another sink, the faster this phase disappears from the soil, the greater the potential mobility of the organics present. However, at closure, the oil phase

TABLE 9.6 RESULTS OF OIL PHASE ANALYSIS FOR A LOAMY SAND

Organic Constituent	Initial Oil Volume (cm)	$t_{1/2,oil}$ (days)	% Leached from ZOI	% Remain in ZOI
naphthalene	0.2	35	0.99	0.0
naphthalene	0.2	350	0.97	0.0
naphthalene	1.5	35	0.82	0.0
naphthalene	1.5	350	0.75	0.0
naphthalene	3.0	35	0.70	0.0
naphthalene	3.0	350	0.59	0.0
phenanthrene	0.2	35	0.23	0.40
phenanthrene	0.2	350	0.22	0.40
phenanthrene	1.5	35	0.20	0.42
phenanthrene	1.5	350	0.17	0.42
phenanthrene	3.0	35	0.18	0.43
phenanthrene	3.0	350	0.13	0.43
chrysene	0.2	35	0.05	1.56
chrysene	0.2	350	0.04	1.56
chrysene	1.5	35	0.04	1.56
chrysene	1.5	350	0.04	1.56
chrysene	3.0	35	0.04	1.56
chrysene	3.0	350	0.04	1.56

present does not consist of the rapidly degrading fractions, since most of these have already disappeared, but rather of the much more slowly degrading compounds. Therefore, the oil phase half-life at closure will be much greater than 35 days. When modeling closure, the best value to use for the oil phase half-life is one determined for the oil phase at the specific site being examined. In a worst case analysis, a short half-life, such as 35 days can be appropriate, and was used in this evaluation.

Degradation Rate Variations - The two variables examined most closely in this research were the degradation rate depth and time constants, γ and ω. These variables can be related to the different closure options. The actual numerical values for these constants are unknown, but it is possible to predict the relative magnitudes of these parameters associated with each of the different closure options. For example, the tilling of a site will promote degradation due to enhanced oxygen availability. Therefore, the option of continued treatment should show less sensitivity to the degradation rate depth constant than the option of leaving the site alone due to the greater oxygen availability at greater depths. Another example is the capping of the site with either a clay or synthetic cap. This type of cap is likely to promote anoxic or anaerobic conditions at the site. Since the anoxic or anaerobic degradation rate usually is less than the aerobic degradation rate, the initial degradation rate is expected to decline with time, and residual organics therefore will remain longer than for an uncapped site.

The following variables were used in this analysis: (a) sandy loam, (b) average annual temperature: 14°C, (c) 50% relative humidity, (d) oil volume: 1.5 cm, and (e) initial concentration: 500 g/m^3. The values for the soil parameters are found in Table 9.1. The values for the temperature and relative humidity were average values for mid-Texas to represent conditions in an area having many refinery HWLT facilities. The f_{oc} and infiltration rates also were varied along with γ and ω. For the f_{oc}, values in the ZOI varied from 0.028 to 0.007, and the values for the LTZ were varied from 0.01 to 0.007. The infiltration was varied according the the scenario examined. For an uncapped site, the infiltration rate ranged from 0.1 to 1.5 m/yr, and for the clay or synthetic cap, the infiltration rates examined were 0.1 and 0.01 m/yr.

To better examine the influence of these variables, the following organics were evaluated: benzene, anthracene, chrysene, and o-xylene. These organics are different from those used in the oil phase parameter analysis and have a wide range of half-lives and partition coefficients. The values used are presented in Table 9.7. For the residual organic half-life, the degradation rate chosen was estimated to be 10% of the initial degradation rate.

TABLE 9.7 FATE AND TRANSPORT VALUES USED IN SENSITIVITY ANALYSIS(5)

Organic Constituent	log K_{oc}	K_O	K_H	$t_{1/2}$ (days)
benzene	1.5	135	0.2	5
anthracene	4.2	1620	0.067	30
chrysene	5.0	2000	0.0	60
o-xylene	2.2	5250	0.22	94

In examining the degradation rate depth constant, γ, the important consideration was the mobility of the organic. The degradation rate was assumed to be constant within the ZOI due to site management practices, and the persistence would not be altered by varying γ. For the purposes of this analysis, a half-depth was defined. As the half-life is the time for the mass of a compound to decrease to one half of its initial value, a half-depth is the depth at which the degradation rate will have decreased to one half of its initial value. Table 9.8 describes the half-depths evaluated, as well as the associated values for γ. The values chosen for the infiltration rate varied from 0.1 to 1.5 m/yr, and the values for the $f_{oc,ZOI}$ ranged from 0.007 to 0.028. The values for the $f_{oc,LTZ}$ were assumed to be 0.01, or the value used for the ZOI, whichever was lower. To better highlight the sensitivity of RITZ to the degradation rate as a function of depth, the degradation rate was assumed not to be a function of time. At most sites, once the acclimation period is complete, the degradation rate will exhibit steady state behavior, and is not likely to be a function of time unless the soil system is altered in some way. For example, if the soil loading exceeds the toxic level for the bacteria, and some of the bacteria are killed, the degradation rate will decrease.

TABLE 9.8 HALF-DEPTHS IN THE LTZ AND ASSOCIATED γ VALUES

Half-depth (m)	γ
0.2	3.47
1.0	1.39
1.5	0.693
2.0	0.347

The organics studied showed almost no sensitivity to the depth variation of the degradation rate. Table 9.9 demonstrates sample results for o-xylene, the most mobile of the organics tested, and an infiltration rate of 1.5 m/yr, the highest infiltration rate tested. The lack of sensitivity is not unreasonable. First, most of the degradation occurs in the ZOI, where the degradation rate is not altered. Second, the organics which do leach are degraded in the top of the LTZ, and do not reach a depth at which the decreasing degradation rate has an effect. These sensitivity runs were conducted with a low but reasonable value for the fraction of organic carbon in the ZOI, 0.028. At land treatment sites where organics have accumulated over time, this value may be much higher.

TABLE 9.9 DEGRADATION RATE DEPTH CONSTANT VARIATION AND o-XYLENE MOBILITY

Degradation Rate Constant (γ)	% Leached from ZOI	% Leached from LTZ
0.0	8.1	0.0
0.347	8.2	0.0
0.693	8.3	0.0
1.39	8.3	0.0
3.47	8.3	0.0

If the fraction of organic carbon is much lower, the retentive capacity of the ZOI would be decreased, and the variation of the degradation rate with depth could become important. The sensitivity runs were repeated with a 1.0 m/yr infiltration rate, and decreasing f_{oc} values to demonstrate this potential. Table 9.10 shows the results of this analysis for o-xylene.

TABLE 9.10 SENSITIVITY OF o-XYLENE MOBILITY TO γ AND f_{oc} VARIATION

Organic Carbon Fraction ($f_{oc,ZOI}$)	Degradation Rate Constant (γ)	% Leached from ZOI	% Leached from LTZ
0.028	0.347	5.4	0.0
0.028	0.693	5.4	0.0
0.028	1.39	5.4	0.0
0.028	3.47	5.4	0.0
0.014	0.347	5.8	0.00001
0.014	0.693	6.1	0.00001
0.014	1.39	6.1	0.00002
0.014	3.47	6.1	0.0001
0.007	0.347	6.4	0.001
0.007	0.693	6.4	0.0012
0.007	1.39	6.4	0.0015
0.007	3.47	6.4	0.0031

The mobility of o-xylene increased as the organic carbon content of the soil decreased. This is evident in the increasing fraction of the mass which leached from the ZOI. The effect of decreasing the degradation rate with depth was magnified in this case because less organic matter was retained in the ZOI, and more leached to the LTZ where the degradation rate decreased.

The sensitivity of RITZ to the degradation rate time variation was examined for both persistence and mobility. At closure of HWLT sites, the only circumstance in which the degradation rate is expected to be a strong function of time is in the case of capping the site with either a clay or synthetic liner. The primary purpose of such a cover is to prevent the water infiltration and the subsequent migration of constituents which are not expected to be contained or degraded in the treatment zone under normal conditions. The purpose in examining the persistence was to determine if the residues remain in the ZOI in measurable quantities for longer than the post-closure period, and are still present when the site is opened for other uses.

The same organics and site parameters were used in this analysis as in the depth variation analysis (Table 9.7) with several exceptions. The infiltration rate will decrease considerably at a capped site, and values of 0.1 and 0.01 m/yr were used. Furthermore, the cap will prevent volatilization at the site, and the Henry's Law constants were set to zero to simulate this change. The value for the degradation rate depth constant, γ, also was set to zero. A "half-time" was defined as the time in which the degradation rate drops to one half of its initial value. By altering the degradation rate time constant (ω), different scenarios can be represented. For example, if a clay cap decreased the degradation rate rapidly, as in several months, the half-time might only be 60 days. For other scenarios, the degradation rate might decrease more slowly, and the half-time might be on the order of a year. The range of values in Table 9.11 covers these scenarios.

TABLE 9.11 HALF-TIMES AND ASSOCIATED ω VALUES

Half-Time (d)	Degradation Rate Time Constant (ω)
60	0.0095
180	0.0038
360	0.0019

The mobility of the compounds with high organic carbon partition coefficients, anthracene and chrysene, were unaffected by varying both the infiltration and the time constant. In all cases, the total mass of these compounds degraded in the ZOI. For benzene, even though some mass, 0.1%, did leach from the ZOI, there was no sensitivity to the time constant. This was due to the rapid decay rate of benzene. The applied mass of benzene degraded too rapidly for the effects of the decreasing degradation rate to be seen. The o-xylene was sensitive to the changing degradation rate. Table 9.12 demonstrates the changing mobility of the o-xylene for the case where the infiltration rate was 0.1 m/yr. The case where the infiltration rate was 0.01 m/yr demonstrated the same trends, but the magnitude of the changes was smaller.

The persistence of all the compounds was affected by the change in the degradation rate with time. This can be seen in Table 9.13 for anthracene and o-xylene, the two most persistent compounds. Benzene was only moderately affected, since, as previously mentioned, its degradation rate was rapid and most of the mass was degraded before the effects of the decreasing degradation rate could be seen. In examining the persistence, an arbitrary value of 0.01 g/m^3 was chosen as the concentration remaining in the ZOI to be compared. This corresponds to about 10 ppb, which is at or below the detection limit for many of the organics of concern. The infiltration rate for these results was 0.01 m/yr. As expected, for a slowly degrading compound, such as in this evaluation o-xylene, the decreasing degradation rate was quite significant, increasing the persistence from approximately 3.5 years to over 25 years. Even for the more rapidly degrading compound, such as in this evaluation anthracene, the change is significant, from 1 year to 8 years. All of the anthracene would likely be gone before the site is opened for other use after a post-closure period of 30 years, but 8 years is still a long time for a constituent to remain.

TABLE 9.12 SENSITIVITY OF o-XYLENE MOBILITY TO DEGRADATION RATE TIME VARIABILITY

ω	% Migrate from ZOI
0.0	0.9
0.0019	2.3
0.0038	5.7
0.0095	13.7

TABLE 9.13 SENSITIVITY OF THE PERSISTENCE OF ANTHRACENE AND o-XYLENE TO THE DECREASE OF THE DEGRADATION RATE WITH TIME

Organic Constituent	Degradation Rate Time Constant (ω)	Time Remain in ZOI (years)
o-xylene	0.0	3.5
o-xylene	0.0019	6.5
o-xylene	0.0038	20
o-xylene	0.0095	25
anthracene	0.0	1.0
anthracene	0.0019	1.7
anthracene	0.0038	4
anthracene	0.0095	8

The implications of the results of these analyses to closure are many. For the options of continued treatment, or a vegetative cap, no time variation in the degradation rate is expected. The degradation rate would be expected to have the normal variation with depth as explained by Jury et al.(46). If the site is left alone, a small variation in the degradation rate with time would be expected due to the discontinuation of management practices, such as tilling. For the option of placing a clay or synthetic cap over the site, the time variability will be the major influence. If the degradation became anaerobic, the variation with depth would not increase significantly, since the oxygen diffusion rate would not be limiting. Based upon the relative magnitudes of the changes associated with each option, values for the degradation rate depth and time constants can be assigned. Table 9.14 summarizes the degradation rate depth and time parameters which can be associated with each closure option. These values are not intended as accurate measures of the changes expected at these sites, but rather as tools for the comparison of the various options.

TABLE 9.14 DEGRADATION RATE DEPTH AND TIME CONSTANTS ASSOCIATED WITH EACH CLOSURE OPTION

Closure Option	γ	ω
Continued Treatment/Vegetative Cap	0.693	0.0
Leave Site Alone	1.39	0.00019
Clay or Synthetic Cap	0.347	0.0095

MINTEQ

The sensitivity of MINTEQ to site parameters influenced by closure options also was examined. These included pH, the presence of organics, the partial pressure of CO_2 gas (PCO_2), and the redox state of the soil solution. MINTEQ output was examined to determine the effects of these parameters on the solubility of the metals contained in the soil solution. The hypothesis was that metals which remain soluble will eventually migrate out of the treatment zone.

The starting point for this analysis was a "generic" soil solution that was adapted from the analysis of a saturation extract for a Holtsville soil(51). The "generic" soil solution used in this evaluation does not necessarily relate to a soil solution or to conditions that may exist at HWLT sites or a site with contaminated soils. The "generic" soil solution was used to have a common, well-defined set of characteristics that could be used to evaluate the sensitivity of MINTEQ to physical and chemical changes that might be expected at closed HWLT sites. The Holtsville data represent a well-documented and comprehensive actual situation and thus real soil solution characteristics.

Table 9.15 describes the composition of this solution. The concentrations in this table, as well as throughout this section are presented as pC values. This nomenclature refers to the negative log of the molar concentration (–log[C]), which can be used to describe the low concentrations found in soil solutions. Using pC values is similar to using pH. A pC of 2, corresponds to a molar concentration of 0.01, while a pC of 8 would correspond to a molar concentration of 1.0×10^{-8}.

TABLE 9.15 SOIL SOLUTION COMPOSITION FOR A HOLTSVILLE SOIL (From Reference 51)

Component	pC	Component	pC
Ca	2.28	Ni	5.99
Mg	2.64	Pb	7.02
Sr	4.20	Cd	7.57
K	2.89	CO_3	2.40
Na	2.00	SO_4	2.12
Fe	5.75	Cl	2.03
Mn	4.66	F	4.15
Cu	5.33	PO_4	4.19
Zn	4.97	NO_3	3.56

The pH of the Holtsville solution was 7.9. The above concentrations were for the total amount of a given component. For example, the value for iron includes Fe^{+3} and Fe^{+2}, as well as all the various species of both redox states of iron. Since MINTEQ does not consider redox equilibria unless specifically told to do so, it was necessary to include both members of a redox pair in the input data for the analyses in which the redox equilibria was not considered. In these cases, the different redox states were treated by MINTEQ as being two different components. In nature, redox reactions are often very slow, being limited by kinetic restraints, and it is possible for two members of a redox pair to exist in solution out of redox equilibrium, but still in chemical equilibrium with the other species present. Therefore, the case where redox equilibria is ignored is still important because it was useful to know how both species will behave under the same set of conditions. The metals for which both redox states were included were iron, copper and manganese. In addition to separating the redox pairs, it was also necessary to add additional components to the solution to include metals which are found in petroleum refinery waste such as vanadium, selenium and chromium. Redox data for vanadium was available in the MINTEQ database, and three redox states, V^{+2}, V^{+3}, and V^{+5}, were included. The redox data for selenium were not available.

Several other assumptions were necessary. Temperature was assumed to be constant and was set at 25°C. Temperature is used in the calculation of activity coefficients which are fairly constant within the temperature ranges found in soils. The ionic strength of the solution was assumed to be constant. The ions with the greatest concentrations, Na^+ and Cl^-, are not affected by speciation, and it is these ions which control the ionic strength of a solution. Another assumption was a choice of PCO2. The PCO2 of the atmosphere is about 0.0003 atm, or 0.03%. The PCO2 of soils usually is higher. At most HWLT sites, during the active life of the site, the land is tilled, and the PCO2 may be only slightly higher than atmospheric. For the situation where a site was tilled, the PCO2 was chosen to be 0.003 atm, or 0.3%.

MINTEQ has the capacity to ignore certain minerals if this is desired by the user. In this research it was necessary to ignore the mineral dolomite. This was due to the presence of both calcite and magnesite, along with dolomite. These three minerals could not exist and simultaneously control the solubility of calcium and magnesium without violating the Gibb's phase rule. This assumption does not alter the calculations since dolomite does not form in solution and precipitate, and therefore does not control the solubility of calcium and magnesium. If dolomite is present in the original mineral composition of the soil it will have some affect on the solubilities, but both calcite and magnesite also will be present.

pH and Organics - In the first analyses, the pH of the solution was varied from acidic to basic. The pH's used were 5, 7.1, and 9. These values simulated the range found in soils. A pH of 7.1 was used to simulate a neutral solution instead of pH 7.0 due to convergence difficulties when a pH of 7.0 was used in MINTEQ. Following the procedure of Morel(52), several organic ligands were added to the solution to examine the changes in the speciation of the metals. The organics were tartrate, humate and fulvate, as these were the only organics in the MINTEQ database found to complex with the metals of interest. These organic ligands were included to simulate the complexing properties of existing ligands in a contaminated soil. Table 9.16 describes the changes in aqueous speciation for the case without organics for metals of interest. Table 9.17 presents the ratio of the soluble metal after speciation to the input concentration. These numbers are only for comparative purposes. It does not make sense to speak of soluble metals in absolute terms, since metals are conservative species, and are considered in terms of concentration. If the input metal concentration is 0.01 M and 0.000001 M metal remains soluble, the soluble fraction is less than 1% of the input, but may still be enough to leach from the site in measurable concentrations. However, considering the fraction of the input that remains soluble does provide a way to compare the changes in solubility for a given metal under different conditions. For example, magnesium is highly soluble at pH 5 and pH 7.1, but is much less soluble at pH 9.

In Table 9.16, it is evident how the metal speciation changes when the pH changes. At higher pH, where the OH^- concentration is higher, more metals are found in hydroxide complexes, which tend to be less soluble than the free metal ions. Furthermore, as the pH becomes more basic, CO_3^{-2} becomes the dominant carbonate form. Many of the $^{+2}$ cations, such as calcium, iron or strontium form carbonate complexes which precipitate. The formation of hydroxide and carbonate complexes are the two most important reasons for the decrease in soluble metal concentrations at high pH. This is evident from Table 9.17, where the solubility of most of the divalent metals has decreased.

There are several other trends worth noting. The metals which exist primarily as anions, such as selenium and chromium, are not affected by the changes in pH. This is important in HWLT, since several of the metals of concern, such as chromium or arsenic, exist primarily as anions. Another point is a comparison of the various redox states of certain metals. For example, Cu^{+1} is much less soluble than Cu^{+2}. If copper is a metal of concern at a given site, it would be useful to promote reducing conditions at the site in order to convert the bulk of the copper to the less soluble Cu^{+1} form. Similar trends are observed for iron and manganese, but it is the more oxidized forms, the trivalent ions which are less soluble.

The next step in the analysis was the addition of the organic ligands. Humate, fulvate and tartrate were added to the model solution at concentrations of 0.0001 M. This concentration assured that the organics would be in excess of the metals and the full effect of the complexation reactions would be seen. These concentrations simulate the large amount of organics which are present in the soil at HWLT sites. The addition of organics only affected copper, lead, cadmium and iron. There are two reasons for this. First, the other metals do not complex with the organics as readily as do these four. Secondly, the MINTEQ database is not complete. The organics present do not simulate every organic which may be present in the soil. Organo-metallic complexes formed by the other metals are not in the database. Table 9.18 lists the major aqueous forms of the metals which complex with the organics.

TABLE 9.16 CHANGES IN METAL SPECIATION AND SOLUBLE METAL FRACTIONS AS A FUNCTION OF pH

Component	Major Aqueous Forms pH = 5	pH = 7.1	pH = 9
Ca^{+2}	Ca^{+2}, $CaSO_4$	Ca^{+2}, $CaSO_4$	Ca^{+2}, $CaSO_4$ $CaCO_3$, $CaHCO_3^+$
Fe^{+2}	Fe^{+2} $FeSO_4$	Fe^{+2} $FeSO_4$	Fe^{+2} $FeSO_4$, $FeOH^+$
Fe^{+3}	$FeOH^{+2}$ $Fe(OH)_2^+$	$Fe(OH)_2^+$ $Fe(OH)_3$	$Fe(OH)_3$ $FeOH_4^-$
Cu^{+1}	Cu^{+1} $CuCl_2^-$	Cu^{+1} $CuCl_2^-$	Cu^{+1} $CuCl_2^-$
Cu^{+2}	Cu^{+2} $CuCl^+$ $CuSO_4$	Cu^{+2} $CuCO_3$ $CuOH^+$	$CuCO_3$ $Cu(CO_3)_2^{-2}$ $Cu(OH)_2$
Ni^{+2}	Ni^{+2} $NiSO_4$	Ni^{+2} $NiSO_4$ $NiCO_3$	$NiCO_3$ $Ni(CO_3)_2^{-2}$
Pb^{+2}	Pb^{+2} $PbCl^+$ $PbSO_4$	Pb^{+2}, $PbSO_4$ $PbCl^+$, $PbCO_3$ $PbOH^+$, $PbHCO_3^+$	$Pb(CO_3)_2^{-2}$ $PbCO_3$
Cd^{+2}	Cd^{+2}, $CdSO_4$ $CdCl^+$	Cd^{+2}, $CdCO_3$ $CdCl^+$	$CdHCO_3^+$, $CdSO_4$ $CdCO_3$
Cr^{+6}	CrO_4^{-2} $HCrO_4^-$	CrO_4^{-2} $HCrO_4^-$	CrO_4^{-2}
Se^{+6}	SeO_4^{-2}	SeO_4^{-2}	SeO_4^{-2}
V^{+2} V^{+3}	V^{+2}, VOH^+ VOH^{+2}, $V(OH)_2^+$ $V(OH)_3$	V^{+2}, VOH^+ $V(OH)_2^+$ $V(OH)_3$	VOH^+ $V(OH)_3$
V^{+5}	$H_2VO_4^{-1}$ H_3VO_4	$H_2VO_4^{-1}$ $H_2VO_4^{-2}$	$HV_2O_7^{-3}$ $H_2VO_4^{-2}$
Mn^{+2}	Mn^{+2}, $MnCl^+$ $MnSO_4$	Mn^{+2}, $MnCl^+$ $MnSO_4$	Mn^{+2}, $MnSO_4$ $MnHCO_3^+$
Zn^{+2}	Zn^{+2}, $ZnSO_4$ $Zn(SO_4)_2^{-2}$	Zn^{+2}, $ZnSO_4$ $Zn(SO_4)_2^{-2}$	$Zn(CO_3)_2^{-2}$

TABLE 9.17 FRACTION OF INPUT METAL CONCENTRATION REMAINING SOLUBLE AFTER SPECIATION

Component	Fraction Remaining Soluble (%)		
	pH = 5	pH = 7.1	pH = 9
Ca^{+2}	100	98	0
Mg^{+2}	100	100	1
Sr^{+2}	100	100	1
Fe^{+2}	100	100	2
Fe^{+3}	0	0	0
Cu^{+1}	0	0	0
Cu^{+2}	100	44	83
Ni^{+2}	100	100	100
Pb^{+2}	37	53	100
Cd^{+2}	100	100	17
Cr^{+6}	100	100	100
Se^{+6}	100	100	100
V^{+2}	100	100	100
V^{+3}	100	75	75
V^{+5}	100	100	100
Mn^{+2}	5	100	0
Zn^{+2}	100	100	100

Humate and fulvate simulate the large chain organics which are contained in soil. Therefore, metals complexed with humate and fulvate will not migrate. For iron, cadmium and copper, the combination of organic complexation and mineral precipitation should hinder migration. Lead is more difficult to predict since the influences of these two attenuating processes overlap at low pH. At any HWLT site the influence of organics is important due to the large amount of organics present. The scope of the organics present in the MINTEQ database is too narrow to accurately model the effect of organics on metal mobility, but does provide a first step in examining this problem. The complexation of metals with soluble low molecular weight organics also can enhance metal mobility.

As the results of this sensitivity analysis and the discussion indicate, without specific information about the metal concentrations and physical and chemical conditions that exist in a soil, the forms of a metal that may be present and the potential of these forms to leach are difficult to predict. Therefore, to predict the potential of metals at a given site, it would be useful to have an accurate representation of the forms of the applied metals.

The organic complexes were less prevalent at pH 9. In basic solutions, the carbonate and hydroxide complexes dominate. There will be greater amounts of metal precipitates as insoluble carbonates and hydroxides, but less complexation as organo-metallic complexes.

Carbon Dioxide - The next phase of the analysis examined the influence of the partial pressure of carbon dioxide gas on the solubility of the metals. The PCO$^{(2)}$ range examined was 0.03, 0.003, and 0.0003 atm, which represent a ten-fold increase and decrease from the PCO$^{(2)}$ used in the previous analysis. Before examining the results, it is useful to review carbonate solution chemistry. Under acidic conditions, H_2CO_3 is the dominant form, with HCO_3^- becoming more prevalent as the pH increases. Near pH 9, there are almost equal amounts of HCO_3^- and CO_3^{-2}. Therefore, since metal ions complex with both HCO_3^- and CO_3^{-2}, the influences of varying the partial pressure of CO_2 should be apparent only at pH 7.1 and pH 9, and should be more dramatic at pH 9.

TABLE 9.18 METAL SPECIATION AS INFLUENCED BY pH AND THE PRESENCE OF ORGANICS

	Major Forms		
Component	**pH = 5**	**pH = 7.1**	**pH = 9**
Fe^{+3}	$Fe(OH)_2^+$ Fe-fulvate Fe-humate	$Fe(OH)_2^+$ $Fe(OH)_3$ $FeOH_4^-$	$Fe(OH)_3$ $FeOH_4^-$
Cu^{+2}	Cu^{+2} Cu-fulvate Cu-humate	Cu^{+2}, Cu-fulvate $CuCO_3$, $Cu(OH)_2$ Cu-humate	$CuCO_3$ $Cu(OH)_2$ $Cu(CO_3)_2^{-2}$
Pb^{+2}	Pb^{+2}, $PbCl^+$ $PbSO_4$ $PbSO_4^{-2}$ Pb tartrate	Pb^{+2}, $PbCl^+$ $PbCO_3$, $PbSO_4$ $PbOH^+$, $PbHCO_3^+$ Pb-tartrate	$Pb(CO_3)_2^{-2}$ $PbCO_3$
Cd^{+2}	Cd^{+2}, Cd-tartrate $CdCl^+$, Cd-humate $CdSO_4$ Cd-fulvate	Cd^{+2}, Cd-tartrate $CdCl^+$, Cd-humate $CdSO_4$ Cd-fulvate	$CdHCO_3^+$ $CdCO_3$

It is necessary to understand the types of mineral phases which control the solubility of a given metal. For metals which exist in solution as cations, such as Fe^{+2}, or Cd^{+2}, the mineral precipitates in soils are usually oxides, hydroxides, or carbonates. Knowing which precipitate a given mineral will form is important. Many divalent cations will precipitate as carbonates, such as calcium (calcite), manganese (rhodocrosite), iron (siderite) and cadmium (otavite). As the concentration of carbonate in solution increases, the concentration of all these ions will decrease, in order to satisfy equilibrium constraints. Some metals do not precipitate as carbonates except at very high concentrations. An example of this is copper carbonate. Cu^{+2} will precipitate as CuO. However, as the carbonate concentration increases, the concentration of $CuCO_3$ and $Cu(CO_3)_2^{-2}$ will increase, while the concentration of Cu^{+2} will decrease. Therefore, an increase in soluble copper is expected since copper will exist as the more soluble carbonate, and not as the less soluble oxide.

The results demonstrate many of the expected trends, but the solution chemistry is too complex for easy explanations. There were no changes evident in the pH 5 runs. This was expected since H_2CO_3 is by far the dominant aqueous form of carbonate, and does not complex with any ions. The effects were more apparent at pH 7.1 and pH 9. Table 9.19 presents the changes in the major solution phase forms of Cu^{+2}, Cd^{+2}, Fe^{+2} and Pb^{+2} for pH 7.1. Table 9.20 presents the same information for pH 9.

The dominant aqueous forms of these metals have shifted to the carbonate complexes. The effect on soluble concentrations can be seen in Figure 9.1 where the fractions of the initial metal concentrations which remain soluble are compared. Copper precipitates as an oxide, and its solubility is enhanced by the formation of soluble carbonate complexes. The solubility of lead is enhanced for the same reason, though lead does not precipitate as an oxide. The solubility of iron is decreased, since iron precipitates as a carbonate. The solubility of cadmium is unaffected.

One condition inherent in MINTEQ is that MINTEQ reports the organo-metallic complexes as part of the aqueous concentration. In reality, many of these complexes are immobile, since the organics are part of the immobile background organic fraction of the soil. Therefore, when an increase in PCO2 causes a shift away from organo-metallic complexes and towards soluble carbonate complexes, the solubility of a metal could be enhanced. For example, for lead at pH 7.1, the decrease in the fraction of lead contained in organo-metallic complexes is probably indicative of an increase in soluble lead concentration, but this is not reported by MINTEQ.

These results have interesting implications for HWLT. If the metals of concern precipitate as carbonates, such as iron, a buildup of CO_2 gas and an increase in pH would be desirable. However, if the metals of concern precipitate primarily as oxides, such as copper, or as metals complexed by organics, the opposite would be true. It is evident from these analyses that the different redox states of the metals exhibit very different behavior in solution.

Redox - Unfortunately, the MINTEQ database is limited. For example, the database does not contain chromium^{+3}. There are several other metals of concern in HWLT which also are not fully represented in the database. However, by examining the redox sensitivity of several metals, some conclusions can be drawn about the redox sensitivity of the model. The metal groups used in the sensitivity analysis were Fe^{+2}/Fe^{+3}, Cu^{+1}/Cu^{+2}, $V^{+2}/V^{+3}/V^{+5}$, and Mn^{+2}/Mn(III).

TABLE 9.19 DOMINANT AQUEOUS FORMS AT pH 7.1 FOR $^{+2}$ FORMS OF COPPER, CADMIUM, IRON AND LEAD AS A FUNCTION OF PCO_2

	Major Aqueous Form		
Ion	**PCO2 = 0.0003 atm**	**PCO2 = 0.003 atm**	**PCO2 = 0.03 atm**
Cu^{+2}	Cu^{+2}, $Cu(OH)_2$	Cu^{+2}, $Cu(OH)_2$	Cu^{+2}, $Cu(OH)_2$
	Cu-fulvate	Cu-fulvate, $CuCO_3$	Cu-fulvate, $CuCO_3$
	Cu-humate	Cu-humate	Cu-humate, $CuHCO_3^+$
Cd^{+2}	Cd^{+2}, $CdCl^+$	Cd^{+2}, $CdCl^+$	Cd^{+2}, $CdCl^+$
	Cd-tartrate, $CdSO_4$	Cd-tartrate, $CdSO_4$	Cd-tartrate, $CdSO_4$
	Cd-fulvate	Cd-fulvate	Cd-fulvate, $CdHCO_3^+$
	Cd-humate	Cd-humate	Cd-humate, $CdCO_3$
Fe^{+2}	Fe^{+2}	Fe^{+2}	Fe^{+2}
	$FeSO_4$	$FeSO_4$	$FeSO_4$
Pb^{+2}	Pb^{+2}, $PbCl^+$	Pb^{+2}, $PbCl^+$	Pb^{+2}, $PbSO_4$
	$PbOH^+$, $PbSO_4$	$PbOH^+$, $PbSO_4$	$PbHCO_3^+$
	$PbCO_3$	$PbCO_3$, $PbHCO_3^+$	$PbCO_3$
	Pb-tartrate	Pb-tartrate	$Pb(CO_3)_2^{-2}$

TABLE 9.20 DOMINANT AQUEOUS FORMS AT pH 9 FOR $^{+2}$ FORMS OF COPPER, CADMIUM, IRON AND LEAD AS A FUNCTION OF PCO_2

	Major Aqueous Form		
Ion	PCO2 = 0.0003 atm	PCO2 = 0.003 atm	PCO2 = 0.03 atm
Cu^{+2}	$CuCO_3$ $Cu(CO3)_2^{-2}$	$CuCO_3$ $Cu(CO3)_2^{-2}$	$CuCO_3$ $Cu(CO3)_2^{-2}$ $Cu(OH)_2$
Cd^{+2}	Cd^{+2}, $CdCl^+$ $CdSO_4$, $CdHCO_3^+$ $CdCO_3$	$CdHCO_3^+$ $CdCO_3$	$CdHCO_3^+$ $CdCO_3$ $Cd(CO_3)_3^{-4}$
Fe^{+2}	Fe^{+2} $FeOH^+$ $FeSO_4$	Fe^{+2} $FeOH^+$ $FeSO_4$	Fe^{+2}, $FeHPO_4$ $FeOH^+$ $FeSO_4$
Pb^{+2}	$PbCO_3$ $Pb(CO_3)_2^{-2}$	$PbCO_3$ $Pb(CO_3)_2^{-2}$	$Pb(CO_3)_2^{-2}$

In examining the redox sensitivity, the important parameter to examine is the total solubility of a metal, i.e., the sum of the solubilities of the two forms. From Table 9.17, the less soluble form of each metal can be predicted. At pH 5, Fe^{+3}, and Cu^{+1} are far less soluble than the other forms of these metals. Both forms of manganese are insoluble, and all forms of vanadium are soluble. In fact, Mn^{+2} is the only aqueous form of manganese. Manganese^{+3} will only exist as a solid. Conditions which favor the formation of Mn^{+3} will greatly reduce manganese solubility. At pH 7.1, the same iron and copper forms are insoluble, while V^{+3} and Mn^{+3} are the less soluble forms. At pH 9, the less soluble forms are Fe^{+2}, Cu^{+1}, V^{+3}, but both iron and manganese forms are relatively insoluble. If the less soluble forms are known, then predictions on total solubility can be made based upon the redox condition of the system. The results of the redox sensitivity are presented in Figure 9.2, where the results are presented as the fraction of the input metal concentration which is still soluble under the given conditions.

The results of this analysis were as predicted for copper and iron. The solubility was controlled by the form which was favored by the redox conditions. The situation with manganese is less straightforward. The reduced form, Mn^{+2}, was favored under

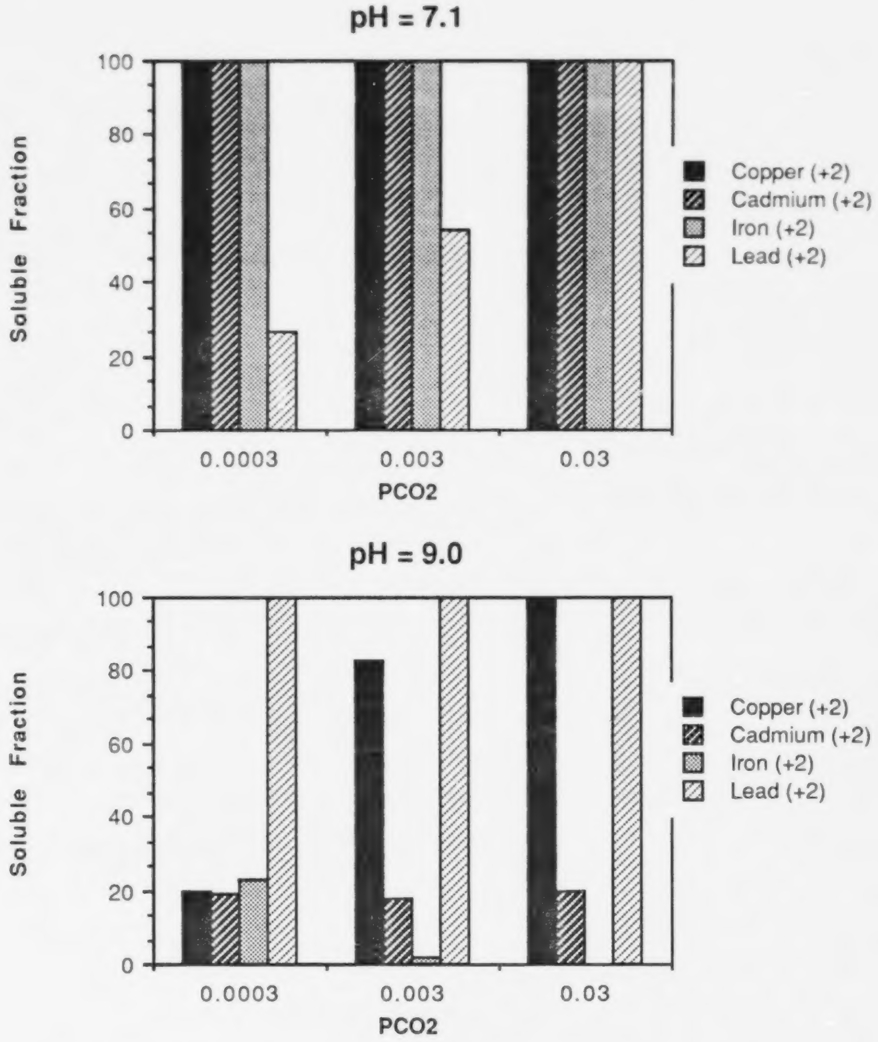

FIGURE 9.1 SOLUBLE FRACTION OF METAL AS A FUNCTION OF pH AND PCO_2

all conditions. This means that the redox equilibria conditions that would favor the oxidation of manganese fall outside the range of redox conditions used in this analysis, and therefore outside the range of redox states found in soils. In soils, manganese will always be found in the reduced form. Vanadium was also more complicated. Vanadium was converted primarily to the most oxidized form, V^{+5}. This form of vanadium is highly soluble under the conditions used in this analysis. Therefore, since the other two forms of vanadium demonstrated high solubility, it is likely that vanadium will be soluble in soils under most conditions.

SUMMARY

The objectives of this evaluation were to examine the mobility of organic and inorganic constituents present in soil at closure of hazardous waste land treatment sites using RITZ for the organics and MINTEQ for the metals. The sensitivity of both classes of constituent to parameters which might be influenced by closure was examined. The purpose of the evaluation was to better understand the environmental impacts of the various closure options.

The input data used for this evaluation were obtained from peer reviewed literature and from studies in which land treatment had been used for wastes similar to those that had been applied to the sites from which samples were taken in this study. For reasons explained in the Introduction to this Section, data obtained from the laboratory studies that were part of this project were not used in this evaluation of the models. The use of reasonable input data and assumptions did allow the objectives of this evaluation to be met, i.e., to determine whether these models are appropriate for predicting or evaluating changes in persistence and mobility of constituents in the accumulated residues in soils at closure and during post-closure.

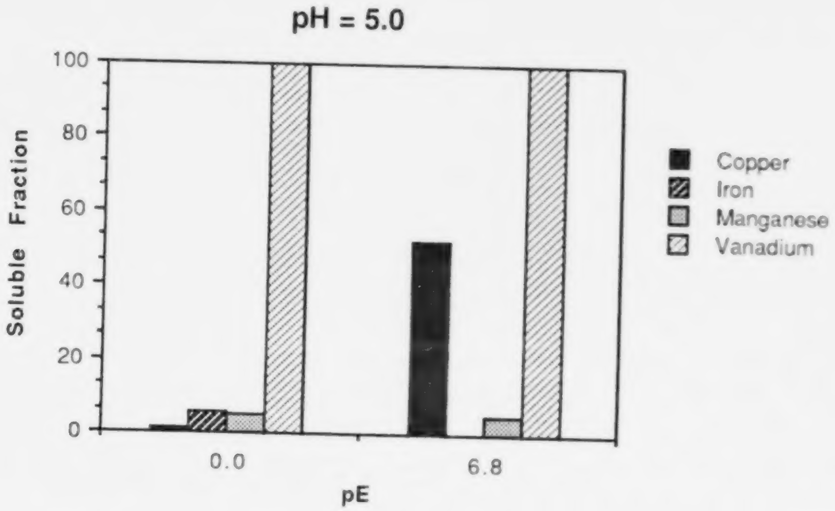

FIGURE 9.2 SOLUBLE METAL CONCENTRATIONS AS A FUNCTION OF pH AND pE

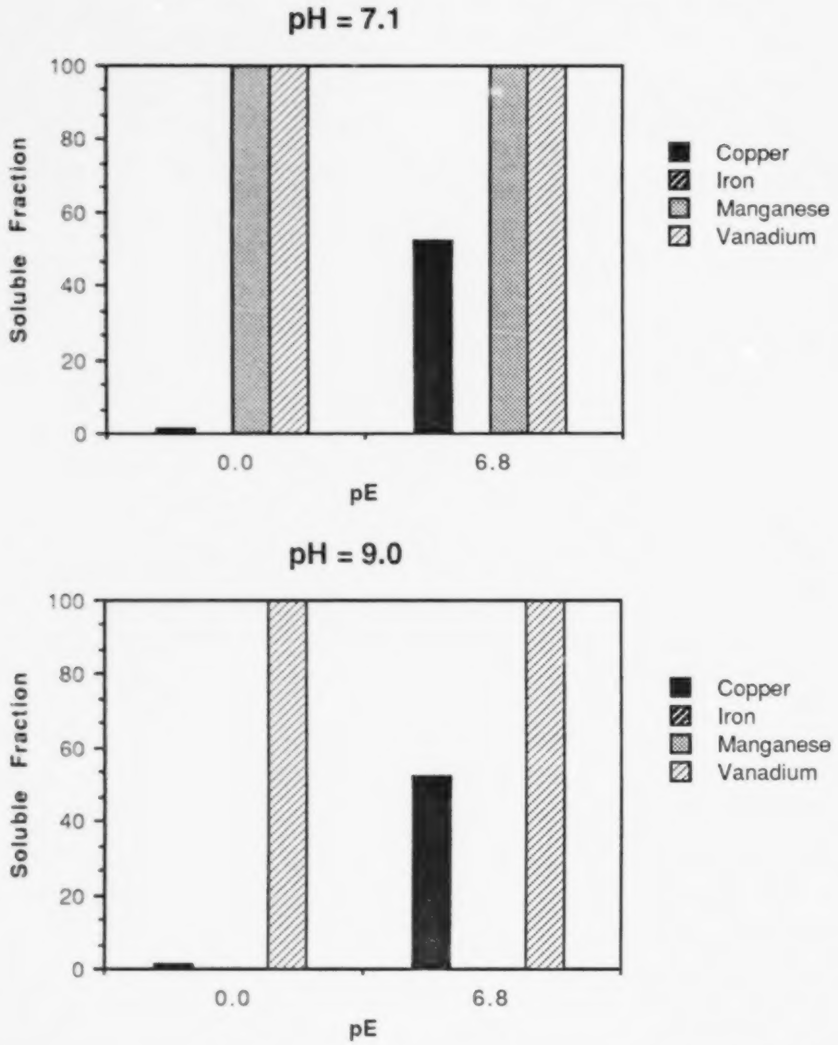

FIGURE 9.2 SOLUBLE METAL CONCENTRATIONS AS A FUNCTION OF pH AND pE, continued

RITZ

The RITZ model was modified to: (a) function with no waste input, (b) consider variations in degradation rate as a function of time, soil depth and aerobic and anaerobic conditions, (c) include the existence of a separate oil phase and the separate degradation of the oil phase, and (d) utilize different chemical partition coefficients in the ZOI and LTZ. The modified model was then used to evaluate its use under conditions likely to occur at HWLT and contaminated soil sites.

RITZ was shown to be insensitive to: (a) changes in relative humidity, (b) changes in temperature within the normal range found at HWLT sites, and (c) the oil phase parameters, both the initial oil content and the oil phase degradation rate. RITZ showed some sensitivity to soil type. The persistence and mobility of the organics were unaffected, but the relative amounts of the organics which degraded and volatilized were altered. Generally, in soil types with less porosity, less water is present in the ZOI. Since volatilization in RITZ is a direct function of the amount of constituent in the aqueous phase, and therefore, the amount of water, there is less volatilization, and more degradation in the soils with lower porosity.

The sensitivity of RITZ to the degradation rate depth and time constants was examined. These parameters were used to simulate the decrease in the degradation rate with time and/or depth. RITZ was relatively insensitive to the depth variation of the degradation rate. Results from the RITZ modeling indicated that almost all of the organics examined were indicated to completely degrade in the ZOI, and not leach into the LTZ where the decreasing degradation rate could be a factor. RITZ was more sensitive to the time variation of the degradation rate. It was assumed under certain circumstances, such as anaerobic conditions being induced by the placement of a clay or synthetic cap over the site, that the degradation rate of the organics would be significantly decreased. Under these conditions, the degradation rate would decrease well before the organic constituents have degraded, and the degradation of the remaining organics would be much slower.

MINTEQ

The sensitivity of MINTEQ was examined for the three most important parameters which are influenced by the closure option, pH, the partial pressure of carbon dioxide gas, and the redox state. It was difficult to draw general conclusions about the effects of these changes, since different metals behave differently in solution. In general, most of the metals present in solution as cations will become less soluble as the pH increases, and as the partial pressure of carbon dioxide increases. This is due to increasing amounts of precipitation as hydroxides and carbonates. No general statements could be made about redox condition, as the most soluble redox state of a given metal varies from metal to metal.

The implications of these results to closure conditions are not clear. Redox equilibria are complicated, and the sensitivity of different metals is hard to predict. Furthermore, it is necessary to know which forms of a given metal are the most soluble. Predictions can be made of metal solubilities for specific sites, when the metals of concern are known, but it is difficult to determine any specific guidance. Based upon this evaluation, the general guidance of maintaining a pH of 6.5 or greater seems valid for most metals of regulatory concern which exist as cations. In terms of the other variables, it is not possible to make *a priori* predictions for the conditions which are least likely to promote metal mobility.

It is possible to relate different site conditions with the different closure options. For continued treatment or a vegetative cap, the site conditions should be oxidizing, and the pH should remain close to the active pH. For the leave-alone option, the redox state should be less oxidizing since the diffusion of oxygen into the soil is decreased. If a clay or synthetic cap is placed over the site, there will be an increase in the partial pressure of carbon dioxide gas and limited oxygen transfer which also should promote reducing conditions.

SECTION 10

MODELING SPECIFIC SITES

INTRODUCTION

As described in Section 9, the modeling efforts that were part of this project were conducted simultaneously with the sample characterization, spatial variability, weathering and degradation studies presented in previous Sections. However, data needed for the modeling efforts were not available from the laboratory studies until very late in the project. Thus, the input parameters to the modeling efforts that were part of this project were not those determined in the laboratory portion of this project. Rather, reasonable values and scenarios applicable to HWLT sites were used for the modeling efforts.

The intent of the effort described in this Section was to illustrate the use of the modified versions of RITZ and MINTEQ models (Section 9) to evaluate HWLT closure options. The modified models were applied to the Texaco, Anacortes refinery waste land treatment site. Considerable data on this site were available to understand and evaluate the applicability of the models and to model potential migration of constituents of the accumulated residues. In addition to using conditions specific to those at Anacortes, conditions typical of other regions of the country also were investigated.

TEXACO ANACORTES

The site chosen to examine the use of the modified models at closure was the Texaco Refinery and Marketing, Inc., site located in Anacortes, Washington. Anacortes is located in northwest Washington, on the Puget Sound. This site has been used to treat refinery wastes for several decades (Section 3). This site was appropriate because of the length of time the site was used and the site data that were available.

Most of the information used in this effort was obtained from the Texaco, Anacortes RCRA Part B Permit application(7) which contained site background information, as well as information about treatability studies and treatability demonstrations. One result of the long-term use of the Texaco site has been the accumulation of waste residues which has raised the land surface about two to three feet (Section 3). This surface buildup added complexity to the modeling effort with RITZ. RITZ is designed for a 5 foot treatment zone. In this analysis, a treatment zone depth of 5 feet was assumed.

Organics

Site Data --

A variety of data is necessary to use the modified RITZ. The first group of data are the soil parameters. Soil cores were taken as part of a 1987 study at the site(7), and soil textures were identified. The soils data were presented for the ZOI, as well as for several different depths in the LTZ. For ZOI values, the reported values were used. For the LTZ, the values for each core were averaged to obtain average LTZ data. The soil textural parameters used in the modeling effort are presented in Table 10.1.

TABLE 10.1 PARAMETERS FOR SOIL TEXTURES PREVALENT AT TEXACO, ANACORTES HWLT SITE

Soil Texture	θ_R	Porosity	ρ_b g/cm^3	ε	K_s (m/d)
Clay	0.106	0.475	1.39	13.7	0.28
Silty clay loam	0.054	0.473	1.40	15.2	0.27
Clay loam	0.087	0.476	1.39	10.7	0.92
Sandy clay loam	0.075	0.406	1.57	8.8	1.19

As part of the 1987 study, several piezometer tests were run. Values for the hydraulic conductivity were reported in the range of 10^{-6} to 10^{-7} cm/sec based upon in-situ piezometer measurements. These are much lower than those estimated with the soil textural classifications. These levels are very low, and little water movement through the soil would be expected. In terms of site specific modeling efforts, these values should be used since they represent actual site data. However, in this modeling effort, since the estimated values (Table 10.1) are much greater, they were used as worst case analyses.

The other soil data required is the fraction of organic carbon, f_{oc}, present in the ZOI and the LTZ. Values for the total organic carbon, TOC, were presented in the 1987 study as percent, and these values were used for the fraction of organic carbon. The range for the f_{oc} in the ZOI was 1.4–13.0%, with an average of 8.6%. For the LTZ, the range was 0.2–2.3%, with an average of 1.1%. To evaluate a worst-case scenario, the lowest reported values for the ZOI and LTZ were used (1.4 and 0.2%, respectively). However, when the conditions for a specific Texaco HWLT plot were evaluated, the actual data for that plot were used in the modeling effort.

The atmospheric and hydrologic parameters used were: (a) mean annual temperature = 10.4°C, (b) mean annual relative humidity = 75%, (c) annual precipitation = 0.68 m/yr, and (d) daily evaporation rate = 2.1 mm/d. The infiltration rate used for the calculations was approximately 30% of the annual infiltration. Values for the daily evaporation rate and mean annual relative humidity were obtained from Climates of the States(48).

For the waste application data, the time of simulation was varied to obtain the most complete accounting for the constituents in the ZOI. Volatile organics and base neutrals in the HWLT soils were measured during the Texaco, Anacortes 1987 study. The range of concentrations for the East plots, the areas from which samples were taken for this analytical and laboratory study, were presented in Table 3.8. However, soils from other Anacortes HWLT plots also were analyzed. For this modeling effort, the maximum concentration of volatile organics and base neutrals that were found in the ZOI samples (0-1 ft) from any of the plots evaluated were used. These maximum concentrations are presented in Table 10.2. The concentrations in Table 10.2 were in soil cores taken from different HWLT plots. Thus, these concentrations are not representative of actual HWLT plot conditions. They were used, however, to represent worst-case conditions.

In RITZ, the concentration units used are grams of organic per cubic meter of soil (g/m^3). To convert the concentrations, the ppm values were multiplied by the bulk density. The converted g/m^3 units also are presented in Table 10.2.

Oil volume data is needed for RITZ. As noted in Section 9, such data is expressed as depth of oil over an area (cm^3/cm^2) and have the units of length (cm). To estimate the initial volume of oil per unit area in the ZOI, data from the 1987 study were used. This study reported the residual oil remaining in various plots in 1987. The values ranged from approximately 10–100 tons/acre. Assuming a density for the oil of 1 g/cm^3, these values were converted to the units of cm used in RITZ. The range of values was approximately 0.2–2.2 cm.

The range of values used in this evaluation for the partition and degradation data for the organic constituents are presented in Table 10.3. Where data were not available, the constituent was not modeled. Where a Henry's Law constant was the only unavailable data, this constant was assumed to be zero. This is a conservative assumption since it assumes that the constituent has no volatilization potential. Any error associated with this assumption would underestimate the migration potential, since the more volatile a compound, the less of it will remain in the soil to leach.

TABLE 10.2 MAXIMUM CONCENTRATION OF VOLATILE ORGANICS AND BASE NEUTRALS IDENTIFIED IN TEXACO, ANACORTES HWLT SITE SOIL CORES(7)

Constituent	Maximum Concentration mg/kg dry weight	Maximum Concentration g/m^3
benzene	7.6	10.6
ethylbenzene	30	42
styrene	1.5	2.1
toluene	42	59
o-xylene	62	87
m&p-xylene	140	196
anthracene	14	20
benzo(a)anthracene	88	123
benzo(a)fluoranthene	52	73
benzo(a)pyrene	61	85
chrysene	220	308
fluoranthene	9.4	13.2
1-methylnaphthalene	78	109
naphthalene	6.6	9.2
phenanthrene	71	99
pyrene	96	134
pyridine	<75	<105
1,4-dioxane	<75	<105

The half-life data ($t_{1/2}$) in Table 10.3 resulted from situations where relatively fresh refinery wastes were being land treated and evaluated. It is recognized that the degradation rates of constituents in residuals at closure will be slower than constituents in fresh wastes, as indicated in Section 9. As noted earlier, the laboratory derived degradation rates (Section 9) were not available when this modeling effort was done. Therefore, the constituent degradation rates actually used in this modeling effort to represent closure scenarios were estimated to be 10% of the degradation rates reported in Table 10.3 for land treatment of fresh refinery wastes. For the purposes of this effort, this was felt to be a reasonable assumption. Subsequently, the degradation studies in Section 8 indicated much lower degradation rates. The sensitivity of RITZ to the residual degradation rate was discussed in Section 9.

For this effort, the oil phase half life was estimated to be 35 days. This rate is reasonable for freshly applied oils(4), and will decline with time. However, since the oil phase is considered by RITZ to be immobile, the oil remaining in the soil will not present a threat to the groundwater. The oil phase is considered by RITZ as another sink for the organics. By choosing the most rapid degradation rate for the oil phase, the result was to underestimate the soils potential to retain the organics, and thus cause an overestimation of the potential migration. The time and depth constants, were varied to approximate the changes to the site created by the closure option. The rationale for choosing these values was discussed in Section 9.

TABLE 10.3 FATE AND TRANSPORT PARAMETERS FOR ORGANIC CONSTITUENTS (ADAPTED FROM API, 1987)(5)

Organic Constituent	Log K_{oc}	K_H	K_O	$t_{1/2}$(days)
benzene	1.49--3.07	0.15–0.24	135	0.1–1.0
ethylbenzene	2.22--3.60	0.26–0.37	620	6.1
toluene	1.57--3.07	0.10–0.28	240	6.4
o-xylene	1.64--3.55	0.22	5250	93.9
m, p-xylene	3.18--3.62	0.1	560	8.5–14.7
anthracene	4.20--4.44	0.067	1620	9–53
benzo(a)anthracene	4.23--6.27	n.a.	2190	41–231
chrysene	4.29--5.20	0	2000	5.5–116
1-methylnaphthalene	4.45--4.69	n.a.	2690	12.6
naphthalene	2.66--3.88	0.017–0.05	170	8--30
phenanthrene	3.77--4.50	0.0017–0.006	1950	23--69
pyrene	4.04--5.11	n.a.	2090	10--100

RITZ Results --

General Site Conditions – In examining the different closure options for the Texaco Anacortes site, the following procedure was used. First, the entire range of constituents was modeled using the worst case values for infiltration and f_{oc}. For the infiltration, the worst case value was chosen to be the average annual rainfall. For the f_{oc}., the values used were the lowest reported as discussed earlier. Separate values for the f_{oc} were used for the ZOI and LTZ. The soil type modeled was a clay loam, the most prevalent soil type at the site. The values used for these soil and hydrologic parameters are presented in Table 10.4.

TABLE 10.4 SOIL AND HYDROLOGIC PARAMETERS USED IN WORST-CASE MODELING EFFORTS

Parameter	Value
porosity	0.476
K_s	0.92 m/d
θ_R	0.087
ε	10.7
f_{oc}, *ZOI*	0.014
f_{oc},*LTZ*	0.002
Avg. Annual Temp.	10.4°C
Daily Evaporation	2.1 mm/d
Infiltration	0.68 m/d

The time of simulation was varied in order to obtain the best final accounting for each of the constituents. The initial concentration for each organic was the maximum value reported (Table 10.2). The values for the constituent properties were the worst case values of those reported in Table 10.3. For the partition coefficients, this was the lowest value reported, while for the half-life, a conservative value was used as discussed earlier. Thus, overall conservative site conditions were used for this evaluation.

The only closure options modeled were the leave-alone option, and the clay or synthetic liner cap option. These options reflect the different conditions that may exist at a closed site (Table 1.2). The clay or synthetic liner cap will minimize infiltration, as well as minimize diffusion of oxygen and other gases in the soil and therefore cause anoxic or anaerobic conditions to occur below the cap. The leave-alone option will allow infiltration to occur and oxygen diffusion into the soil thereby enhancing oxidative conditions in the ZOI and some of the deeper soils. The other options, continued treatment, and the vegetative cap option will produce changes in the ZOI and LTZ soils that will be similar to those caused by the leave-alone option. Therefore, if the modeling indicates no potential problem with the leave-alone option, the same result should occur with these other two options.

The results of the modeling of the site for the leave-alone option are presented in Table 10.5. Table 10.5 does not account for the total mass of the organics. There are minor mass balance differences which are due mainly to rounding off of numbers and to possible volatile loss (Section 9). For this evaluation, these errors are not critical, since the major concern is migration potential. The purpose of this effort was to determine if a constituent would migrate below the treatment zone depth, rather than the exact mass that will do so.

TABLE 10.5 MODELING OF THE TEXACO, ANACORTES SITE FOR THE LEAVE-ALONE CLOSURE OPTION

Organic Constituent	% Degrade In ZOI	% Leach From ZOI	% Leach From LTZ
benzene	63.6	3.7	0.0
ethylbenzene	75.4	1.1	0.0
toluene	72.4	3.2	0.0
o-xylene	40.1	6.6	0.01
m, p-xylene	87.5	0.7	0.0
anthracene	93.2	0.3	0.0
benzo(a)anthracene	98.6	1.4	0.0
chrysene	99.2	0.6	0.0
1-methylnaphthalene	100	0.0	0.0
naphthalene	83.1	5.4	0.0
phenanthrene	97.4	1.1	0.0
pyrene	99.0	1.0	0.0

The results of modeling the leave-alone option with worst-case parameters indicated a very slight potential for only one constituent, o-xylene, to migrate from the LTZ. If this potential is considered important then this constituent should be evaluated on a plot by plot basis, in order to better determine its migration potential under parameters that more closely represent actual conditions.

The other closure option modeled was capping the site with a clay or synthetic liner. As with the leave-alone option, worst case parameters were used in these evaluations. The values used for the soil and hydrologic parameters were the same as those listed in Table 10.4, except for the value for infiltration, which was reduced to a low value to account for the effect of the cap. The other values which differed from the modeling of the leave-alone option were the Henry's Law constants. These values were set to zero since volatilization is very low for this option. The degradation rate was assumed to be a function of time, and ω was set equal to 0.0095, which predicts a decrease in the degradation rate in a matter of several months.

When examining the clay or synthetic cap option, another important environmental parameter is the time that a constituent remains in the ZOI. When a closed site is opened at a future time, if specific constituents continue to be present, a potential threat to human health and the environment might exist. The persistence of the constituents was compared in terms of the time required for the concentration of the constituent in the ZOI to drop a very low value, below 0.01 g/m^3.

Table 10.6 lists the results for the clay or synthetic cap option and an infiltration rate of 1% of the annual infiltration, or 0.0068 m/yr. The amount of constituents that was estimated to migrate from the ZOI under these worst-case conditions was very small, except for the o-xylene. None of the constituents modeled were indicated to migrate from the LTZ. The cap did succeed in preventing migration out of the treatment zone. However, the persistence of several of the constituents was very high, with both the chrysene and benzo(a)anthracene indicated to remain for about 30 years. Whether the existence of these constituents would prevent future use of the land would have to be considered as part of a closure decision.

TABLE 10.6 MODELING OF THE TEXACO, ANACORTES SITE FOR THE CLOSURE OPTIONS OF A CLAY OR SYNTHETIC CAP

Organic Constituent	% Leach from ZOI	% Leach from LTZ	Time in ZOI (days)
benzene	0.1	0.0	100
ethylbenzene	0.01	0.0	200
toluene	0.0	0.0	200
o-xylene	7.2	0.0	>15 years
m, p-xylene	0.01	0.0	720
anthracene	0.01	0.0	15 years
benzo(a)anthracene	0.1	0.0	>30 years
chrysene	0.03	0.0	30 years
1-methylnaphthalene	0.0	0.0	1100
naphthalene	0.1	0.0	1100
phenanthrene	0.1	0.0	20 years
pyrene	0.05	0.0	20 years

Plot Specific Conditions – The modeling evaluation described above was done for general worst-case site conditions. However, actual rather than worst-case conditions and parameters exist in each treatment plot at the Texaco, Anacortes site. To evaluate the applicability of RITZ to plot specific conditions and to determine if a chemical such as o-xylene would migrate from the ZOI and LTZ of specific plots, soils data from the land treatment plots that contained o-xylene were used.

Site soil characterization data indicated that o-xylene was only found in 5 plots in the 1987 study(7). Table 10.7 lists those sites, as well as the plot specific parameters necessary to model potential migration in these plots. The fraction of organic carbon in the ZOI of these plots was much greater than the worst case value, and the retentive capacity of such soil therefore will be much greater. Modeling parameters other than those noted in Table 10.7 were the same as those used in the worst case analysis.

TABLE 10.7 PLOT-SPECIFIC PARAMETERS USED FOR MODELING OF o-XYLENE MOBILITY AT THE TEXACO, ANACORTES SITE

Plot	Concentration (g/m^3)	Soil Texture	f_{oc}, ZOI	f_{oc}, LTZ	Oil Volume (cm)
9-B	0.39	clay loam	0.112	0.003	1.1
10-W	0.85	clay loam	0.051	0.007	1.1
11-A	86.8	clay loam	0.130	0.012	1.8
11-B	44.8	clay	0.130	0.010	1.8
11-C	0.29	clay loam	0.099	0.009	1.8

In the plot-specific modeling of the leave-alone option, the higher values for the fraction of organic carbon in the ZOI were large enough to retain the o-xylene in the treatment zone until it could be degraded (Table 10.8). Even in this analysis, some of the chemical leached (migrated) from the ZOI but not from the LTZ.

Summary – The results of the worst-case site conditions and actual plot specific conditions indicate that under the closure conditions and for the chemicals modeled, there should be no migration of the chemicals through the LTZ. The results also indicate that the clay or synthetic liner cap option may result in some residual organic constituents persisting at a closed site for decades.

TABLE 10.8 PLOT-SPECIFIC MODELING OF o-XYLENE AT THE TEXACO, ANACORTES SITE – LEAVE-ALONE CLOSURE OPTION

Plot	% Degrade In ZOI	% Leach from ZOI	% Leach from LTZ
9-B	77.9	5.9	0.0
10-W	75.4	6.5	0.0
11-A	87.0	5.5	0.0
11-B	95.4	5.5	0.0
11-C	88.1	5.0	0.0

Metals

Data--

The data available for modeling the potential mobility of the inorganic constituents at the Texaco Anacortes site are more limited than that for the organics. There are no soil solution data, though soil pore samples were taken. The only data which are useful are the soil pH, which ranged from 5.2 to 6.7 in the background plots and the plots to which hazardous wastes have been applied. There were no redox data available for the site. The average temperature of the site was 10.4°C. Since the partial pressure of carbon dioxide was unknown, a value of 0.003 atm was used, which is slightly higher than atmospheric.

To model inorganic mobility at the site, the same soil solution identified in Table 9.14 was utilized as the starting point. To better model the Texaco residues, the input data were adjusted to encompass the metals present at the site. The main metals modeled were those contained in the Texaco waste streams. In addition, the total metals data from the part B permit application(7) were checked. Any metals noted as being found anywhere in the site in higher than background concentrations also were considered. These were arsenic and mercury. Table 10.9 contains the metals examined in this analysis, as well as the different redox states included in the input data for each metal.

The range of pH values used was 5.2, 6.0, 6.4, and 6.7. The background pH in the top 1.5 meters was 5.2 to 6.4, and that for the hazardous waste plots was 6.0 to 6.7. This is a narrow range of pH, and the local variability between sample locations could account for a large amount of this differential. The pE range used was 0.0 and 6.8, which covers a reasonable range of pE values expected in soils. The above conditions were analyzed to examine changes in the metal solubilities.

TABLE 10.9 METALS MODELED AT THE TEXACO, ANACORTES SITE

Metal	Redox States
Arsenic	As^{+3}, As^{+5}
Chromium	Cr^{+6}
Lead	Pb^{+2}
Mercury	Hg^{+1}, Hg^{+2}
Nickel	Ni^{+2}
Vanadium	V^{+2}, V^{+3}, V^{+5}

MINTEQ Results --

The results did not demonstrate many differences between the different closure options. For three of the metals, chromium, nickel and vanadium, there was no difference between any of the scenarios examined. As discussed in Section 9, chromium is only listed in the MINTEQ database in the $^{+6}$ oxidation state, which exists in solution as the anion, $Cr_2O_4^{-2}$. This form of chromium is highly soluble and is not sensitive to the changes in solution characteristics found in soil solutions. In reality, chromium will exist primarily as Cr^{+3}, except under highly oxidizing conditions, and will be far less soluble than was predicted for Cr^{+6}. Nickel also was not sensitive to the changes in solution characteristics, and remained soluble under all conditions. Under the redox conditions common in soils, vanadium is present as V^{+5}, which is found in highly soluble forms in soil solutions.

Arsenic and lead and mercury exhibited different sensitivities to the changes in site conditions. Arsenic can precipitate at the higher pH values. Under oxidizing conditions and acidic pH, arsenic exists primarily as As^{+3}, which does not precipitate, while under reducing conditions, the primary form is As^{+5}, which can precipitate as $Ba_3(AsO_4)_2$. This precipitate also occurs under oxidizing conditions and higher pH, which results in a decrease in arsenic solubility at pH 6.4 and 6.8, even at a pE of 0.0. Since only one redox state of lead was modeled, it was not expected that lead would be overly sensitive to redox state, and it was not.

Based upon these results, continued treatment would be a likely closure option, but any option which maintained a pH of 6.0 or greater will be protective of human health and the environment. Several of the metals, especially nickel, may be mobile under any closure scenario.

OTHER SITES

The evaluation for the Texaco Anacortes site illustrated the effect of closure options for the soil type and weather of one HWLT site. To expand the understanding of the modified RITZ to estimate closure scenarios, conditions at two other geographical locations also were modeled. These were locations that are known to have petroleum industry HWLT facilities. These additional locations were on the east coast in southern New Jersey, and in the gulf coast near Lake Charles, Louisiana. To make a comparison, it was assumed that, except for weather and soil conditions, the data from the Anacortes site, such as chemical concentrations, were applicable at these hypothetical locations. Each site was modeled for the leave-alone option, as well as the clay or synthetic cap option. For the capping option, the infiltration was assumed to be 1.0% of the annual precipitation for the respective sites.

The additional climatic site data necessary for this evaluation were obtained from Climates of the States(48). The soil types were estimated based upon the prevalent soil types documented in the soil surveys of the counties (or parishes) in which the hypothetical sites were located. For the New Jersey site, the following data were used, based upon the climate of Atlantic City: (a) average annual precipitation: 1.16 m/yr, (b) average annual temperature: 12.1°C, and (c) soil texture: sandy loam. For the Louisiana site, the following parameters were used based upon the climate of Lake Charles: (a) average annual precipitation: 1.41 m/yr, (b) average annual temperature: 20.2°C, and (c) soil texture: silt loam.

Organics

As with the Texaco Anacortes site, the worst case infiltration was assumed to be the average annual precipitation for the leave-alone option. The relative humidity was assumed to be 50%, since the RITZ model is insensitive to variations in the relative humidity. Tables 10.10 and 10.11 present the results for the New Jersey site for the leave-alone and clay/synthetic cap options, respectively, and Tables 10.12 and 10.13 present the results for the Louisiana site.

TABLE 10.10 MODELING OF A HYPOTHETICAL NEW JERSEY HWLT SITE FOR THE LEAVE-ALONE CLOSURE OPTION

Organic Constituent	% Degrade In ZOI	% Leach From ZOI	% Leach From LTZ
benzene	79.3	12.7	0.0
ethylbenzene	86.0	2.9	0.0
toluene	85.1	8.1	0.0
o-xylene	57.3	13.3	0.01
m, p-xylene	89.1	5.0	0.0
anthracene	93.1	1.8	0.0
benzo(a)anthracene	98.4	3.1	0.0
chrysene	99.4	4.0	0.0
1-methylnaphthalene	100	0.4	0.0
naphthalene	85.1	15.6	0.0
phenanthrene	97.6	6.9	0.0
pyrene	99.2	1.6	0.0

The results are fairly similar for all the sites. In a worst-case analysis, the leave-alone option was satisfactory for all the constituents except o-xylene. As with the

Anacortes site, the clay or synthetic cap option increased the persistence of the organics in the soil.

TABLE 10.11 MODELING OF A HYPOTHETICAL NEW JERSEY HWLT SITE FOR THE CLAY OR SYNTHETIC CAP CLOSURE OPTION

Organic Constituent	% Leach From ZOI	% Leach From LTZ	Time In ZOI
benzene	0.1	0.0	40 days
ethylbenzene	0.0	0.0	80 days
toluene	0.0	0.0	100 days
o-xylene	10.7	0.0	>12 years
m, p-xylene	0.0	0.0	2 years
anthracene	0.0	0.0	10 years
benzo(a)anthracene	0.1	0.0	>40 years
chrysene	0.0	0.0	>30 years
1-methylnaphthalene	0.0	0.0	1.2 years
naphthalene	0.2	0.0	3.5 years
phenanthrene	0.1	0.0	>15 years
pyrene	0.1	0.0	30 years

TABLE 10.12 MODELING OF A HYPOTHETICAL LOUISIANA HWLT SITE FOR THE LEAVE-ALONE CLOSURE OPTION

Organic Constituent	% Degrade In ZOI	% Leach From ZOI	% Leach From LTZ
benzene	93.7	17.0	0.0
ethylbenzene	96.0	4.1	0.0
toluene	95.3	11.2	0.0
o-xylene	76.4	30.2	0.09
m, p-xylene	96.6	7.6	0.0
anthracene	97.7	2.9	0.0
benzo(a)anthracene	97.9	6.0	0.0
chrysene	99.1	6.9	0.0
1-methylnaphthalene	99.9	0.4	0.0
naphthalene	90.8	21.7	0.0
phenanthrene	98.4	12.6	0.0
pyrene	98.8	2.9	0.0

TABLE 10.13 MODELING OF A HYPOTHETICAL LOUISIANA HWLT SITE FOR THE CLAY OR SYNTHETIC CAP CLOSURE OPTION

Organic Constituent	% Leach From ZOI	% Leach From LTZ	Time In ZOI
benzene	0.0	0.0	45 days
ethylbenzene	0.0	0.0	80 days
toluene	0.0	0.0	90 days
o-xylene	12.2	0.0	>12 years
m, p-xylene	0.0	0.0	2.2 years
anthracene	0.0	0.0	10 years
benzo(a)anthracene	0.1	0.0	>40 years
chrysene	0.0	0.0	>30 years
1-methylnaphthalene	0.0	0.0	1.2 years
naphthalene	0.2	0.0	3.4 years
phenanthrene	0.1	0.0	>17 years
pyrene	0.1	0.0	30 years

The results in these tables for these hypothetical New Jersey and Louisiana sites were obtained using general worst-case site conditions. As was done at Anacortes, data specific to actual HWLT plots also was used in the modified RITZ. Plot-specific analyses did demonstrate the adequacy of the leave-alone option for o-xylene. These results are presented in Table 10.14 for the New Jersey site, and Table 10.15 for the Louisiana site, using the same plot specific Texaco Anacortes data described in Table 10.7. For plot 10-W at the Louisiana site, there was a slight amount of leaching from the LTZ. However, the initial concentration in plot 10-W was only 0.85 g/m^3. The amount that leached was 0.001% of this mass, or approximately 0.85 ppb. This amount of leaching is below the analytical detection limit for the chemical.

TABLE 10.14 PLOT-SPECIFIC MODELING OF o-XYLENE MOBILITY AT A HYPOTHETICAL NEW JERSEY HWLT SITE

Plot	% Degrade In ZOI	% Leach From ZOI	% Leach From LTZ
9-B	62.5	17.7	0.0
10-W	62.0	18.6	0.0
11-A	78.8	15.4	0.0
11-B	78.8	15.4	0.0
11-C	78.0	13.4	0.0

TABLE 10.15 PLOT-SPECIFIC MODELING OF o-XYLENE MOBILITY AT A HYPOTHETICAL LOUISIANA HWLT SITE

Organic Constituent	% Degrade In ZOI	% Leach From ZOI	% Leach From LTZ
9-B	82.6	17.3	0.0
10-W	79.7	18.1	0.001
11-A	92.1	11.2	0.0
11-B	92.1	11.2	0.0
11-C	90.4	12.6	0.0

There are some differences between the modeling results for the different sites. The major differences occur in comparing the various locales for the leave-alone option. Table 10.16 compares the percentages of the organic which leached from the ZOI for each of the different locations. The relevant trends are apparent. The differences are due to the differences in the infiltration. When more water is present, more of the organic constituent is able to leach in the aqueous phase. This can be seen by noticing that it is the organics with the lowest partition coefficients, and therefore the greatest concentration in the aqueous phase, which demonstrate the greatest differences. The three organics with the lowest partition coefficients are benzene, toluene, naphthalene and o-xylene.

The differences between the sites for the clay or synthetic cap closure option were minimal. This is because the clay or synthetic cap greatly decreases the infiltration.

In general, it appears that the more appropriate closure option for most HWLT sites will be the option of continued treatment. This option will continue the conditions which maximize the treatment potential of the site. Other appropriate options include the vegetative cap and the leave-alone options, because these will promote aerobic conditions, which are necessary to maintain a more rapid degradation rate. The remaining options, the clay or synthetic cap, or the removal of contaminated soil are appropriate only for circumstances where infiltration must be reduced. Soil removal is only necessary when it has been shown that there is a large potential for migration, and none of the other closure options will be protective of human health and the environment. The disadvantages of the clay cap are related to the possibility of extremely long persistence of the organics in the ZOI. The longer the organics are present, the longer a potential threat will exist.

TABLE 10.16 COMPARISON OF ORGANIC MOBILITY FOR THE THREE LOCATIONS -- LEAVE-ALONE OPTION

Organic Constituent	% Leach From ZOI		
	Washington	New Jersey	Louisiana
benzene	3.7	12.7	17.0
ethylbenzene	1.1	2.9	4.1
toluene	3.2	8.1	11.2
o-xylene	6.6	13.3	30.2
m, p-xylene	0.7	5.0	7.6
anthracene	0.3	1.8	2.9
benzo(a)anthracene	1.4	3.1	6.0
chrysene	0.6	4.0	6.9
1-methylnaphthalene	0.0	0.4	0.4
naphthalene	5.4	15.6	21.7
phenanthrene	1.1	6.9	12.6
pyrene	1.0	1.6	2.9

Metals

Because of the difficulties of using MINTEQ to model metal mobility at HWLT sites, no comparison to other locations was attempted.

SUMMARY

This section considered the application of RITZ and MINTEQ to specific situations to evaluate their use for closure decisions and to identify the relative environmental effect of closure options. The evaluation indicated the following.

RITZ

The modified RITZ was used to estimate the potential mobility and persistence of organics at a HWLT site under different closure scenarios. When used with worst-case Texaco Anacortes HWLT site data (Table 10.2) at three different locations, the modified RITZ indicated major differences between the capped and uncapped scenarios. The closure options in which the sites were uncapped allowed for aerobic conditions, but the movement of the constituents into the LTZ was greater. For the clay or synthetic cap option, reduced conditions should occur and the movement into the LTZ was greatly diminished, due to the lack of infiltration created by the cap.

At the uncapped site, the persistence, i.e., potential residence times, of organics was approximately 20 years for benzo(a)anthracene, and 1100 days for chrysene and pyrene. For the capped site, 8 of the 12 PAH compounds examined remained in the site for 1100 days or more, and 6 of the 12 remained in the site for 15 years or more. The sensitivity of the modified RITZ model to the differences between the various uncapped closure options was minimal, since the bulk of the degradation took place in the ZOI, and the depth constant did not alter these results. These differences are portrayed in Table 10.17.

The results obtained on the mobility and persistence of organics at a HWLT site under closure scenarios indicated that the modified RITZ can be a useful tool for assessing the impact of different closure options on the migration potential and persistence of residual organics at such sites.

MINTEQ

MINTEQ is able to estimate aqueous equilibrium solubility concentrations for metals but is unable to estimate the actual mobility of metals. Gaps in the MINTEQ database do not allow it to identify the relative solubility of many of the metals of interest at HWLT sites. This evaluation indicated that MINTEQ is useful in demonstrating the potential mobility of metals as indicated by the relative solubility of metal species. MINTEQ cannot be used to determine the closure option most preventative of metal migration, however it can be used to determine the metals most likely to migrate, and a closure plan can be developed to reduce the migration of these specific metals.

The option of capping a site will hinder migration by not allowing water to percolate through the soil. However, metals that remain soluble can move when the site is opened for other uses after the post-closure period has ended.

Closure Options

The results obtained provide insight into the environmental effect of various closure options. There is no "best" option for every situation. The most appropriate option appears to be one in which the site is left without an impermeable cap, i.e., open to the atmosphere. The option of continued management, i.e., tilling, moisture control and possible adding nutrients, is beneficial because the degradation rate of the organics will be greater than the degradation under an impermeable cap.

This was illustrated when the Texaco Anacortes site was modeled. For the organics, no leaching was predicted for the uncapped site, and for the metals, there was no significant increase in metal solubility under oxidizing conditions. The results for the capped site indicated that the residual organics persisted for a long time.

TABLE 10.17 COMPARISON OF PERSISTENCE AND MOBILITY OF ORGANICS PRESENT AT THE TEXACO, ANACORTES SITE AS INFLUENCED BY THE CLOSURE OPTION

Organic Constituent	Leave-Alone % Leach From ZOI	Leave-Alone Time in ZOI (days)	Clay/Synthetic Cap % Leach from ZOI	Clay/Synthetic Cap Time in ZOI (days)
benzene	3.7	32	0.1	100
ethylbenzene	1.1	71	0.0	200
toluene	3.2	55	0.0	200
o-xylene	6.6	146	7.2	>15 years
m, p-xylene	0.7	610	0.0	720
anthracene	0.3	720	0.0	15 years
benzo(a)anthracene	1.4	>20 years	0.1	>30 years
chrysene	0.6	1100	0.0	30 years
1-methylnaphthalene	0.0	240	0.0	1100
naphthalene	5.4	450	0.1	1100
phenanthrene	1.1	720	0.1	20 years
pyrene	1.0	1100	0.1	20 years

Two important results were generated from the evaluation in this Section. One is that the potential persistence and mobility of the accumulated residue constituents are affected by the closure option chosen. Another is that RITZ and MINTEQ, when modified to represent closure conditions, can estimate the potential mobility and persistence of metals and organics for different closure options. The actual choice of a closure option will be dependent on such estimates as well as on operational factors and regulatory concerns.

SECTION 11

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